Supporting Information

# Pyrrolinium-substituted Persistent Zwitterionic Ferrocenate Derivative Enabling the Application of Ferrocene Anolyte

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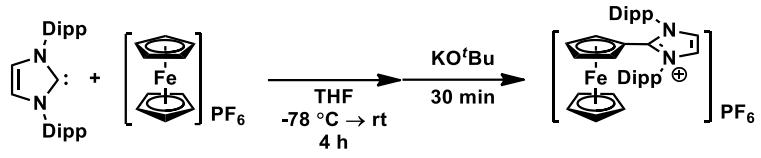
# Table of Contents

## Materials and Methods

All air- and moisture-sensitive manipulations were performed using oven-dried or flame-dri ed glassware, including basic Schlenk and glovebox techniques under $N_2$ atmosphere. Tetr ahydrofuran (THF) were distilled from deep purple sodium benzophenone ketyl. Chlorofor m-$d_1$ was dried using activated molecular sieves 3 Å. *I*Pr and $^{Me}$cAAC was prepared according to the literatures.[1], [2] $FcPF_6$ was prepared according to the literature.[3] DMPZ was purchased from TCI Chemicals (Japan). Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) were purchased from Sigma–Aldrich and dried under vacuum at 180°C for 24 h to remove moisture. All other chemicals were purchased fr om commercial sources and used as received. All deutrated solvents were purchased from Aldrich and Cambridge Isotope Laboratories. NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500 MHz, and 125 MHz for $^1$H and $^{13}$C acquisitions, respec tively. Chemical shifts were referenced to the residual proton solvent peaks ($^1$H: $CDCl_3$, $\delta$ 7.26) and $^{13}$C solvent signals ($CDCl_3$, $\delta$ 77.16).[4] Signals are listed in ppm, and multiplici ty identified as s = singlet, br = broad, d = doublet, t = triplet, m = multiplet; coupling constants in Hz; integration. The microporous separator (Celgard 4560) was purchased from Wellcos (Korea). Purified compounds were further dried under high vacuum (0.01–0.05 Tor r). Yields refer to purified and spectroscopically pure compounds.

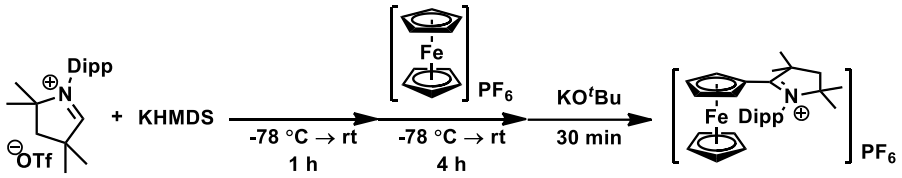
## Experimental Details

**Synthesis of [Fc-IPr]$PF_6$ (1a)**




In a $N_2$ atmosphere glovebox, ferrocenium hexafluorophosphate ($FcPF_6$, 3.31 g, 10 mmol) was placed with THF (50 mL) in a 250 mL round bottom flask under -78 °C. The solution of 1,3-bis-(2,6-diisopropylphenyl)imidazolylidene (*I*Pr, 3.89 g, 1.0 eq.) in THF (100 mL) was added to the flask at –78 ºC. The reaction mixture was warmed to room temperature, and stirred for 4 h. To remove the imidazolium side product, potassium tert-butoxide (1.12 g, 1.0 eq.) was added to the reaction mixture. After 30 min, the solvent was removed under high vacuum and the solid was washed by toluene. The residual solid was purified by silica column chromatography using DCM elute to obtain reddish brown solid. (**1a**, 2.00 g, 56 % yield) The single crystals suitable for X-ray analysis were obtained by the recrystallization in THF using vapor diffusion of pentane at room temperature. NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC): δ = 7.68 (t, J = 7.86 Hz, 2H), 7.64 (s, 2H), 7.45 (d, J = 7.85 Hz, 4H), 4.39 (t, J = 1.98 Hz, 2H), 4.11 (s, 5H), 3.69 (t, J = 1.98 Hz, 2H), 2.46 (m, 4H), 1.26 (d, J = 6.75 Hz, 6H), 1.25 (d, J = 6.75 Hz, 6H), 1.09 (d, J = 6.85 Hz, 6H), 0.82 (d, J = 6.85 Hz, 6H) ppm. $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$, 23 ºC) δ = 148.48, 145.28, 132.68, 132.14, 126.97, 125.55, 72.10, 70.24, 68.19, 66.32, 29.47, 25.49, 22.72 ppm. Anal. Calcd. for $C_{37}H_{45}N_2FePF_6$: C, 61.84; H, 6.31; N, 3.90; found: C, 60.94; H, 6.00; N, 3.81.

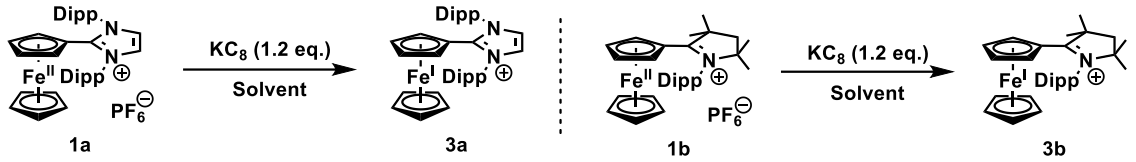
**Synthesis of [Fc-cAAC]$PF_6$ (1b)**




In a $N_2$ atmosphere glovebox, [$^{Me}$cAACH]OTf (4.0 g, 9.2 mmol) was placed with THF (20 mL) in a 40 mL vial and potassium hexamethyldisilazane solution (KHMDS 0.5 M in THF, 18.4 mL, 1.0 eq.) was added to the vial at -78 °C. The reaction mixture was warmed to room temperature, and stirred for 1 h. After 1 h, the cAAC solution was slowly added to the ferrocenium hexafluorophosphate ($FcPF_6$, 3.0 g, 1.0 eq.) which was placed with THF (100 mL) in a 250 mL round bottom flask under -78 °C. After 4 h, to remove the iminium side product, potassium tert-butoxide (1.04 g, 1.0 eq.) was added to the reaction mixture. After 30 min, the solvent was removed under high vacuum and the solid was washed by toluene. The residual the solid was purified by silica column chromatography using dichloromethane/methanol (95:5) elute to obtain deep purple solid. (**1b**, 1.32 g, 46 % yield). The single crystals suitable for X-ray analysis were obtained by the recrystallization in THF using vapor diffusion of pentane at room temperature. NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC): 7.54 (br, 1H), 7.34 (br, 2H), 4.97 (br, 2H), 4.46 (br, 5H), 4.37 (br, 2H), 2.59 (br, 2H), 2.55 (br, 2H), 1.93 (br, 6H), 1.48 (br, 6H), 1.31 (br, 6H), 0.99 (br, 6H). $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$, 23 ºC) δ = 198.42, 145.32, 131.93, 131.65, 126.85, 78.90, 74.88

(br), 73.13, 68.46, 51.93, 50.41, 33.04, 29.51, 29.08, 26.03, 24.75 ppm. Anal. Calcd. for $C_{30}H_{40}NFePF_6$: C, 58.55 H, 6.55 N, 2.28; found: C, 59.96 H, 6.92 N, 2.55. **HRMS (FAB)**: m/z calculated for $C_{30}H_{40}NFePF_6$ $[M\text{-}PF_6]^+$ 470.2510, found 470.2512.

**Synthesis of Fc-IPr/cAAC radical (2a/2b)**




In a $N_2$ atmosphere glovebox, **1a** (72 mg, 0.1 mmol)/**1b** (62 mg, 0.1 mmol) and $KC_8$ (1.2 eq.) were placed in a 4 mL vial and subsequently solvent (benzene, toluene, or $Et_2O$) 10 mL was added to the vial. The reaction mixture was stirred at room temperature. After 30 min, the color of the solution was changed to deep green (**2a**) and deep purple (**2b**). The graphite and remained insoluble starting material of the resulting solution was filtered off with celite. The large amount of $Et_2O$ solvent of the **2a** and **2b** solution was removed by simple vaporization and the remained solvent was finally removed under vacuum to obtain the isolated solid product of **2a** (25 mg, deep green, 44% yield) and **2b** (47 mg, deep purple, 99% yield). Elemental analysis of **2a** and **2b** was not successful due to their high instability under air. The purity of **2a** and **2b** was characterized by $^{57}$Fe Mossbauer spectroscopy. As a result, unlike **2b**, **2a** contained 8.7% of **1a** due to its thermodynamic instability (**Figure S18** and **S19**).

## X-ray Crystallographic Analysis

CCDC 1940623 and 1940622 contains the structural information for **1a** and **1b**. These data can be obtained free of charge via www.ccdc.ac.uk/cgi-bin/catreqcgi (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax (+44) 1223-336- 033; or deposit@ccdc.cam.ac.uk).

**X-ray crystal structure determination of 1a.**

A light brown crystal (0.2 × 0.1 × 0.1 $mm^3$) was coated with paraton oil and mounted on a Bruker APEX-II CCD diffractometer equipped with a graphite-monochromated Mo Kα ($\lambda$ = 0.71073 Å) radiation source at room temperature. The crystal was kept at 100.0 K during data collection. The data were corrected for Lorentz and polarization effects (SAINT), and multi-scan absorption corrections based on equivalent reflections were applied (SADABS). Using Olex2[5], the structure was solved with the ShelXT[6] structure solution program using Intrinsic Phasing and refined with the ShelXL[7] refinement package using Least Squares minimisation. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added to their geometrically ideal positions. SQUEEZE (from PLATON) was used to calculate the electron count in the void space and to get a new HKL file.

**Table S1. Crystal data and structure refinement for 1a.**

| | |
|---|---|
| Identification code | p21n_sq |
| Empirical formula | $C_{37}H_{45}F_6FeN_2P$ |
| Formula weight | 718.57 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 11.8618(4) |
| b/Å | 12.6648(4) |
| c/Å | 27.0687(9) |
| α/° | 90 |
| β/° | 101.713(2) |
| γ/° | 90 |
| Volume/$Å^3$ | 3981.8(2) |
| Z | 4 |
| $\rho_{calc}g/cm^3$ | 1.199 |
| $\mu/mm^{-1}$ | 0.472 |
| F(000) | 1504.0 |
| Crystal size/$mm^3$ | 0.2 × 0.1 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.074 to 52.044 |
| Index ranges | $-14 \le h \le 14$, $-15 \le k \le 15$, $-33 \le l \le 33$ |
| Reflections collected | 117096 |
| Independent reflections | 7855 [$R_{int}$ = 0.0965, $R_{sigma}$ = 0.0428] |
| Data/restraints/parameters | 7855/0/432 |
| Goodness-of-fit on $F^2$ | 1.027 |

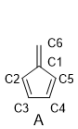
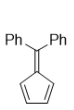
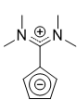
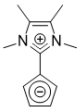
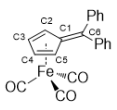
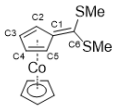
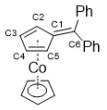
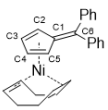
| | |
|---|---|
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0467, $wR_2$ = 0.1082 |
| Final R indexes [all data] | $R_1$ = 0.0658, $wR_2$ = 0.1180 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.55/-0.40 |

**X-ray crystal structure determination of 1b.**

A purple crystal (0.1 × 0.02 × 0.02 mm$^3$) was coated with paratone-*N* oil and the diffraction data measured at 100 K with synchrotron radiation ($\lambda$ = 0.70000 Å) on a ADSC Quantum-210 detector at the Pohang Accelerator Laboratory (2D SMC), Korea. The ADSC Q210 ADX program[8] was utilized for data collection (detector distance is 63 mm, omega scan; $\Delta\omega$ = 1º, exposure time is 20 sec per frame) and HKL3000sm (Ver. 703r)[9] was used for cell refinement, reduction and absorption correction. Using Olex2[5], the structure was solved with the ShelXT[6] structure solution program using Intrinsic Phasing and refined with the ShelXL[7] refinement package using Least Squares minimisation. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added to their geometrically ideal positions.

**Table S2. Crystal data and structure refinement for 1b.**

| | |
|---|---|
| Identification code | c2c |
| Empirical formula | $C_{30}H_{40}F_6FeNP$ |
| Formula weight | 615.45 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 14.958(3) |
| b/Å | 13.919(3) |
| c/Å | 27.339(6) |
| α/° | 90 |
| β/° | 93.73(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 5680(2) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.439 |
| μ/mm$^{-1}$ | 0.648 |
| F(000) | 2576.0 |
| Crystal size/mm$^3$ | 0.1 × 0.02 × 0.02 |
| Radiation | synchrotron (λ = 0.70000) |
| 2Θ range for data collection/° | 4.886 to 67.488 |
| Index ranges | ? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l ≤ ? |
| Reflections collected | 26808 |
| Independent reflections | 8149 [$R_{int}$ = 0.031, $R_{sigma}$ = 0.0274] |
| Data/restraints/parameters | 8149/0/369 |
| Goodness-of-fit on F$^2$ | 1.107 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0765, $wR_2$ = 0.2364 |
| Final R indexes [all data] | $R_1$ = 0.0807, $wR_2$ = 0.2422 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.70/-0.94 |

| |  A |  B |  C |  D |  E |  F |  G |  H |
|---|---|---|---|---|---|---|---|---|
| C1-C2 (Å) | 1.470 | 1.471 | 1.431 | 1.417 | 1.477 | 1.454 | 1.460 | 1.46 |
| C2-C3 (Å) | 1.355 | 1.337 | 1.363 | 1.374 | 1.414 | 1.403 | 1.410 | 1.39 |
| C3-C4 (Å) | 1.476 | 1.454 | 1.416 | 1.41 | 1.399 | 1.421 | 1.409 | 1.43 |
| C4-C5 (Å) | 1.355 | 1.341 | 1.388 | 1.381 | 1.414 | 1.418 | 1.415 | 1.39 |
| C5-C1 (Å) | 1.470 | 1.466 | 1.431 | 1.422 | 1.477 | 1.458 | 1.455 | 1.46 |
| **C1-C6 (Å)** | **1.348** | **1.356** | **1.407** | **1.43** | **1.357** | **1.373** | **1.389** | **1.37** |
| **BLA ($10^{-2}$ Å)** | **11.9** | **11.9** | **4.0** | **2.1** | **5.6** | **4.6** | **3.7** | **6.7** |

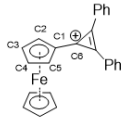
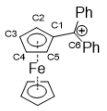
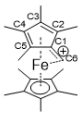
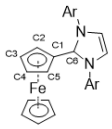
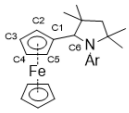
| |  I |  J |  K |  **1a** | **2a** |  **1b** | **2b** |
|---|---|---|---|---|---|---|---|
| C1-C2 (Å) | 1.453 | 1.438 | 1.45 | 1.449 | 1.459 | 1.451 | 1.454 |
| C2-C3 (Å) | 1.432 | 1.413 | 1.38 | 1.420 | 1.427 | 1.416 | 1.425 |
| C3-C4 (Å) | 1.442 | 1.425 | 1.46 | 1.425 | 1.425 | 1.425 | 1.424 |
| C4-C5 (Å) | 1.418 | 1.402 | 1.42 | 1.420 | 1.428 | 1.415 | 1.424 |
| C5-C1 (Å) | 1.453 | 1.445 | 1.42 | 1.449 | 1.458 | 1.457 | 1.456 |
| **C1-C6 (Å)** | **1.445** | **1.416** | **1.37** | **1.455** | **1.406** | **1.447** | **1.421** |
| **BLA ($10^{-2}$ Å)** | **1.8** | **2.6** | **5.3** | **0.9** | **2.7** | **1.8** | **2.1** |

**Figure S1**. BLA parameters of simulated **1a**, **2a**, **1b**, and **2b** at B3PW91/Def2-SVP with selected crystallographic data examples of fulvene and zwitterionic derivatives,[10] low-valent metal-fulvene complexes,[11] ferrocenyl carbocations.[12]

# DFT Calculation

## General information

Density functional theory (DFT) calculations were performed using Gaussian09.[13] Geometry optimizations were carried out using the atomic coordinates of the structures generated by Chem3D (CambridgeSoft Corp., MA). The nature of all stationary points calculated from full optimizations was confirmed *via* frequency analysis, which revealed zero and one imaginary frequency for ground and transition state (TS), respectively. The unrestricted wave function was used for the singlet ground state of *I*Pr, $^{Me}$cAAC, ferrocene, each intermediates, TS, and products. All geometry optimizations were performed using the B3PW91[14] with Def2-SVP basis set,[15] followed by frequency calculations on each optimized structure. Solvation free energies were computed on gas phase-optimized geometries using SMD model of Cramer and Truhlar. [16]

## Proposed Reaction Mechanisms

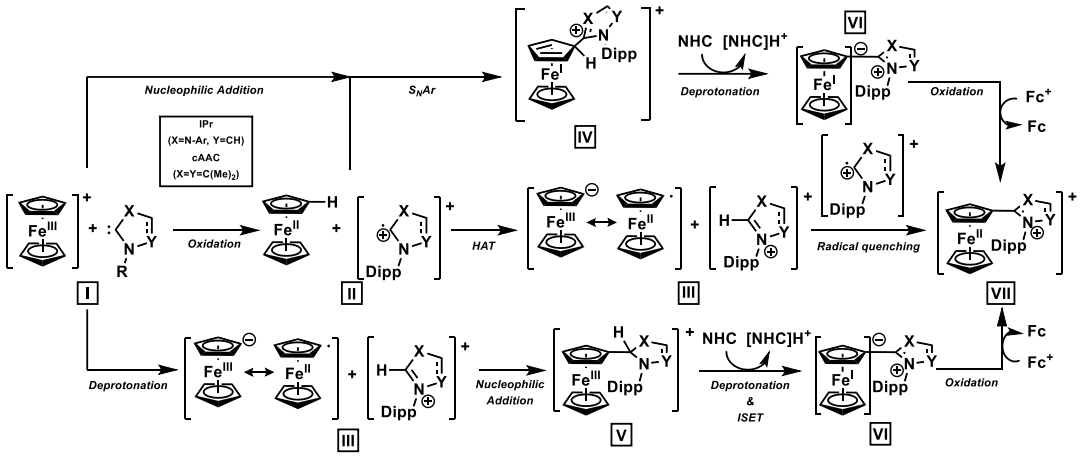



**Figure S2**. Four possible reaction mechanisms of the reaction between ferrocenium and NHCs

## Energy Diagram of the All Possible Reaction Mechanisms

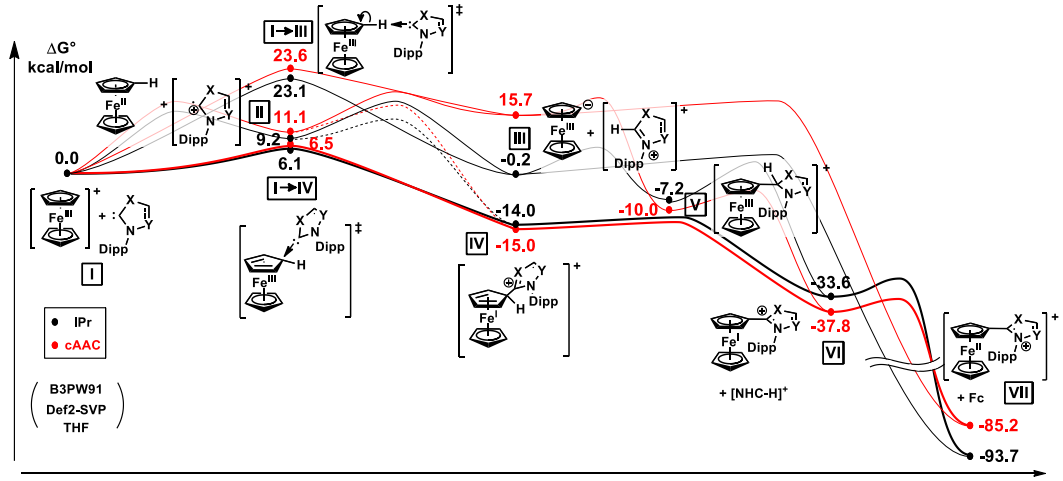



**Figure S3**. Full Energy diagram of four possible reaction mechanisms

**Coordinates of Optimized Structures**

The optimized geometries were displayed in Cartesian coordinates (atomic unit). E° represents 'total electronic energy' and G° represents 'standard Gibbs free energy' in Hartree unit. $E°_{(THF)}$ represent 'total electronic energy' in THF solvent. For transition states, *v* represents the first and only negative imaginary frequency in $cm^{-1}$ unit.

Coordinates of Optimized Structures of Ferrocene

E° = -1650.2634716; G° = -1650.127696; $E°_{(THF)}$ = -1650.2753819

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.3481789975 | -1.3800614104 | 0.6812032174 | H | -1.4836745002 | -2.381947416 | 0.2739969449 |
| C | -1.5323883089 | 0.8972950094 | 1.0172722326 | H | -1.8336871478 | 1.9394152045 | 0.9115681203 |
| C | -0.5563149292 | 0.3945248317 | 1.9290490283 | H | 0.01844463 | 0.9855294862 | 2.6419445998 |
| C | -0.4427635273 | -1.0130006243 | 1.7216852898 | H | 0.2345258688 | -1.685246749 | 2.2482124453 |
| C | 0.5562309402 | -0.3947346338 | -1.9288410589 | H | -0.0186451869 | -0.9858924376 | -2.6415156234 |
| C | 0.4428126868 | 1.012862804 | -1.7218919725 | H | -0.2344034675 | 1.6850352846 | -2.248607846 |
| C | 1.3482925011 | 1.3801505067 | -0.6815459735 | H | 1.4839327547 | 2.3821582169 | -0.2746887419 |
| C | 2.0214672105 | 0.1994923689 | -0.2456516 | H | 2.7611634824 | 0.1415636133 | 0.5527917877 |
| C | 1.5322868033 | -0.8973216599 | -1.0169446989 | H | 1.8334614643 | -1.9394428904 | -0.9108975195 |
| Fe | 0.0000047085 | 0.0001660788 | 0.0000430608 | H | -2.7611162873 | -0.1412110601 | -0.5528148069 |
| C | -2.0214466978 | -0.1993345234 | 0.2456391145 | | | | |

Coordinates of Optimized Structures of Ferrocenium

E° = -1650.002584; G° = -1649.867613; $E°_{(THF)}$ = -1650.0802706

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.3660858417 | -1.3851561118 | 0.6975505502 | H | -1.4982698233 | -2.3866774157 | 0.2870354737 |
| C | -1.5507406435 | 0.8945540374 | 1.0341898454 | H | -1.8488602023 | 1.937794307 | 0.925369702 |
| C | -0.5736514711 | 0.3912512072 | 1.9469640407 | H | 0.0046786352 | 0.9831910329 | 2.6569706704 |
| C | -0.4597892156 | -1.0177247811 | 1.7392154276 | H | 0.2211227332 | -1.6894739218 | 2.2627504765 |
| C | 0.5734017187 | -0.3915158923 | -1.9466150033 | H | -0.0051479609 | -0.9836173817 | -2.6563062099 |
| C | 0.45995253 | 1.0175921161 | -1.7395259292 | H | -0.2208145221 | 1.6892956001 | -2.2633100447 |
| C | 1.366428014 | 1.385265162 | -0.6981144198 | H | 1.4989012708 | 2.3869455717 | -0.2880791272 |
| C | 2.0402201919 | 0.2033473263 | -0.2616570646 | H | 2.7769872581 | 0.1447159425 | 0.5401117421 |
| C | 1.5504311158 | -0.894655928 | -1.0336723048 | H | 1.8482945422 | -1.9379191553 | -0.9243863577 |
| Fe | 0.0000081423 | 0.0003621139 | 0.0000916588 | H | -2.7768907234 | -0.1443688229 | -0.5401870152 |
| C | -2.0401697483 | -0.2032060066 | 0.2616088891 | | | | |

Coordinates of Optimized Structures of $CpFe(C_5H_4)$

E° = -1649.5709896; G° = -1649.446603; $E°_{(THF)}$ = -1649.582903

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.3960293013 | -1.2636093575 | 0.5460610395 | C | 2.0339859197 | 0.247251577 | -0.320092896 |
| C | -1.5497504176 | 1.0201749062 | 0.852966012 | C | 1.5438340168 | -0.8508013561 | -1.0931534673 |
| C | -0.6044368631 | 0.5118416298 | 1.7931537467 | Fe | -0.0076850729 | 0.0905139268 | -0.1239759426 |
| C | -0.510216689 | -0.8991686242 | 1.6036142978 | C | -2.0387526004 | -0.0772434399 | 0.0817308138 |
| C | 0.573657656 | -0.3543666525 | -2.0221512244 | H | -1.5375930286 | -2.267675203 | 0.1466662562 |
| C | 0.4838062451 | 1.0429553398 | -1.7892279435 | H | -1.8287219616 | 2.0656766492 | 0.7250760247 |
| C | 1.375564333 | 1.4408760531 | -0.7590083285 | H | -0.035854148 | 1.1007188928 | 2.5126064399 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 0.1451775184 | -1.5761511286 | 2.1515048419 | H | 2.7600415202 | 0.1757992598 | 0.4909419214 |
| H | -0.0004461179 | -0.9423038284 | -2.7376596169 | H | 1.8366641804 | -1.8939907785 | -0.9666967691 |
| H | 1.5116338179 | 2.4437331595 | -0.355233506 | H | -2.7548760073 | -0.0142330253 | -0.7371186998 |

Coordinates of Optimized Structures of *I*Pr

E° = -1158.8469535; G° = -1158.341263; $E°_{(THF)}$ = -1158.8754004

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.675977222 | -0.060088363 | 1.873769152 | H | 6.1334525062 | -0.5159845234 | -0.9587092195 |
| C | -0.676406014 | 0.0600828235 | 1.8736115335 | H | -4.7020511291 | 2.5333778979 | -0.867741856 |
| N | -1.0583088217 | 0.0928554097 | 0.536331678 | H | -5.1990053439 | -1.7035110231 | -0.3805352832 |
| N | 1.0581916121 | -0.0928437321 | 0.5365790476 | H | -6.1332645252 | 0.5160081783 | -0.9599938631 |
| C | 0.0000437783 | 0.0000304739 | -0.3260977223 | H | -1.6050159871 | -2.2182671342 | 0.6366976872 |
| C | 2.4255249873 | -0.2042959585 | 0.116269785 | H | -2.2121928884 | -2.8334935663 | -1.6922875418 |
| C | 2.93663822 | -1.4777323389 | -0.2122070582 | H | -2.2789579331 | -4.2420923998 | -0.6016507117 |
| C | 3.2204925814 | 0.9581390983 | 0.0615945415 | H | -3.7829673722 | -3.4607914372 | -1.1364112898 |
| C | 4.2791722626 | -1.5615998706 | -0.6007144425 | H | -3.280147564 | -2.3027399463 | 2.4923074213 |
| C | 4.5594276651 | 0.8179569755 | -0.327061243 | H | -4.43492054 | -3.1294452711 | 1.4235847263 |
| C | 5.0863816342 | -0.4274825877 | -0.6550245854 | H | -2.9081920903 | -3.9267389774 | 1.862342956 |
| C | -2.4255485622 | 0.2043034695 | 0.1157116555 | H | -1.1851878345 | 2.494792066 | 0.4301377083 |
| C | -2.9365797395 | 1.4777341731 | -0.2129166104 | H | -3.1547289273 | 3.7357070692 | 1.3996139689 |
| C | -3.2205231277 | -0.9581234484 | 0.0609260699 | H | -2.0355022524 | 4.7785844504 | 0.486820581 |
| C | -4.2790358587 | 1.5616060551 | -0.6016897211 | H | -3.5816793414 | 4.3040444906 | -0.2322995001 |
| C | -4.5593828485 | -0.8179347985 | -0.327988479 | H | -0.9643261409 | 2.1367364887 | -1.9989510652 |
| C | -5.0862523262 | 0.4274992281 | -0.6561091484 | H | -2.3569889142 | 3.2102457284 | -2.3140041475 |
| C | -2.6694357118 | -2.3378171045 | 0.3867368832 | H | -0.8594493459 | 3.8783990891 | -1.6149774356 |
| C | -2.7414558616 | -3.2681387288 | -0.8309064176 | H | 1.6048057337 | 2.2182683478 | 0.6368588448 |
| C | -3.3622101185 | -2.9549268496 | 1.6085235995 | H | 2.2128538762 | 2.8336960835 | -1.6918595344 |
| C | -2.0573937125 | 2.7181022034 | -0.2038005839 | H | 2.279188026 | 4.2421813732 | -0.6010518118 |
| C | -2.7506094122 | 3.9451528518 | 0.3964057973 | H | 3.7834068559 | 3.4609706288 | -1.1353310287 |
| C | -1.5279623077 | 3.0016208236 | -1.6173349524 | H | 3.2792502099 | 2.3025736261 | 2.4930909275 |
| C | 2.6693175746 | 2.3378237405 | 0.3872904621 | H | 4.43447127 | 3.1292524417 | 1.4248366717 |
| C | 2.7417869041 | 3.2682590145 | -0.8302339488 | H | 2.9076398089 | 3.9266378599 | 1.863096326 |
| C | 3.3616800535 | 2.9548092467 | 1.6093782913 | H | 1.1851039996 | -2.4947979222 | 0.4304622539 |
| C | 2.0574601556 | -2.7181103646 | -0.2032680378 | H | 3.1544311671 | -3.7356831615 | 1.4004194434 |
| C | 2.7505516874 | -3.9451441248 | 0.3971175839 | H | 2.0354389975 | -4.7785887 | 0.4873690397 |
| C | 1.528361209 | -3.0016603457 | -1.6169209818 | H | 3.581776613 | -4.3040224355 | -0.2313888314 |
| H | 1.3887131999 | -0.1246017155 | 2.6924267219 | H | 0.964812422 | -2.1367877175 | -1.9986925777 |
| H | -1.3893367496 | 0.1245788272 | 2.6921008579 | H | 2.3575533412 | -3.2102951903 | -2.3133901914 |
| H | 4.7022504845 | -2.5333754096 | -0.8666516213 | H | 0.8598506286 | -3.8784405914 | -1.6147036605 |
| H | 5.1990446152 | 1.7035415039 | -0.3795351127 | | | | |

Coordinates of Optimized Structures of *I*PrH$^+$

E° = -1159.2952747; G° = -1158.7788; $E°_{(THF)}$ = -1159.3733436

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.6781045407 | -0.0750126242 | 1.7788992011 | C | 2.9420333827 | -1.5664653547 | -0.2159270286 |
| C | -0.6797498015 | 0.0746263114 | 1.7788507022 | C | 3.2075945093 | 0.9056957679 | -0.2021201451 |
| N | -1.0827764346 | 0.1187111338 | 0.4604141512 | C | 4.2687478494 | -1.671273601 | -0.6515451306 |
| N | 1.0812363489 | -0.118994541 | 0.4604912132 | C | 4.5263387905 | 0.731469375 | -0.6391216545 |
| C | -0.0007388861 | -0.0001091643 | -0.3161889578 | C | 5.0513707399 | -0.5388878936 | -0.8613600069 |
| C | 2.4456150924 | -0.2640278832 | -0.0056303501 | C | -2.4471207079 | 0.2637581143 | -0.0058043482 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.9435588943 | 1.5661998766 | -0.2160367722 | H | -2.1738767293 | -2.6977416126 | -2.054809745 |
| C | -3.2090508257 | -0.905969909 | -0.2024459882 | H | -2.2635087815 | -4.154083323 | -1.0316916683 |
| C | -4.2702423709 | 1.6710039636 | -0.6517513728 | H | -3.7511768362 | -3.3437785365 | -1.5557046385 |
| C | -4.5277648564 | -0.7317475496 | -0.6395395732 | H | -3.3561096248 | -2.3850618413 | 2.1352423664 |
| C | -5.0528157269 | 0.5386123427 | -0.8617185383 | H | -4.4730586829 | -3.1415491691 | 0.9800201135 |
| C | -2.6718801437 | -2.3071976978 | 0.0489449368 | H | -2.9678906631 | -3.9719417578 | 1.4253421255 |
| C | -2.7169795922 | -3.1685421142 | -1.2204722096 | H | -1.1053921507 | 2.5191938685 | 0.3228386477 |
| C | -3.4081628852 | -2.9850220081 | 1.2133548325 | H | -2.7783307172 | 3.0957856685 | 2.0913258724 |
| C | -2.118707465 | 2.8240642719 | 0.0137863511 | H | -2.0577080342 | 4.5459941302 | 1.3488452526 |
| C | -2.6979742685 | 3.6710705668 | 1.1558397239 | H | -3.7038978211 | 4.0462835514 | 0.9102572363 |
| C | -1.9687542906 | 3.6450566121 | -1.2741209787 | H | -1.5323445985 | 3.0495414458 | -2.0912433806 |
| C | 2.6704508581 | 2.3069226678 | 0.0493367086 | H | -2.9391165838 | 4.0284316191 | -1.6262844832 |
| C | 2.715677047 | 3.1683592417 | -1.2200132899 | H | -1.3166482973 | 4.5153510074 | -1.1008494191 |
| C | 3.406671971 | 2.9846345678 | 1.2138506634 | H | 1.6118091806 | 2.2214206268 | 0.3445754134 |
| C | 2.1171225131 | -2.8243212023 | 0.0137285743 | H | 2.1726173821 | 2.6976414937 | -2.0544256572 |
| C | 2.6962511477 | -3.6714212904 | 1.1557829369 | H | 2.2622306372 | 4.1539041649 | -1.031193573 |
| C | 1.9672683551 | -3.6452230727 | -1.2742479746 | H | 3.749905731 | 3.3435795224 | -1.5551571495 |
| H | 1.3902140012 | -0.1532551903 | 2.5964053074 | H | 3.3545233703 | 2.3846110568 | 2.1356916324 |
| H | -1.3919248172 | 0.1527984085 | 2.5963063114 | H | 4.4715921196 | 3.1411341903 | 0.9806083443 |
| H | -0.0006952428 | -0.0000690486 | -1.4040682281 | H | 2.9664241566 | 3.9715575143 | 1.4258737727 |
| H | 4.6980676013 | -2.6603000715 | -0.8290165708 | H | 1.1037858634 | -2.5194388645 | 0.322701185 |
| H | 5.1556941357 | 1.609002201 | -0.8064986869 | H | 2.7765211636 | -3.0962055648 | 2.0913191025 |
| H | 6.0846415589 | -0.6478487105 | -1.2011391353 | H | 2.0559455216 | -4.5463447802 | 1.3486574266 |
| H | -4.6995776013 | 2.6600320323 | -0.8291773136 | H | 3.7021927877 | -4.0466374086 | 0.9102793694 |
| H | -5.1570813238 | -1.6092848035 | -0.8070376555 | H | 1.530955642 | -3.0496403729 | -2.0913729488 |
| H | -6.0860628442 | 0.647570471 | -1.2015707804 | H | 2.9376518174 | -4.0286068518 | -1.6263435462 |
| H | -1.6132632433 | -2.22167821 | 0.3442689122 | H | 1.3151179264 | -4.5155077624 | -1.1010954877 |

Coordinates of Optimized Structures of *I*Pr$^+$

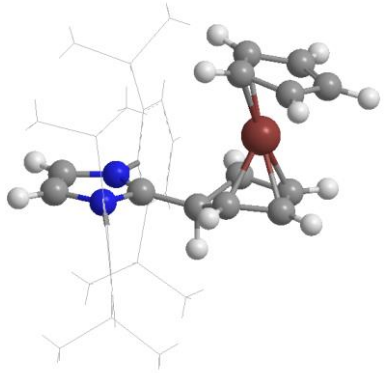
E° = -1158.5855437; G° = -1158.082705; E°$_{(THF)}$ = -1158.663541

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.6787112903 | -0.0693703407 | 1.8508978492 | C | -2.1112447622 | 2.8041895032 | -0.0225155808 |
| C | -0.6786638155 | 0.0692956092 | 1.8509194552 | C | -2.7393316084 | 3.7625513031 | 0.9983016954 |
| N | -1.0934008193 | 0.11067911 | 0.5228786178 | C | -1.8604360572 | 3.4993655988 | -1.3682179016 |
| N | 1.0934116426 | -0.1106973737 | 0.5228433441 | C | 2.6821013323 | 2.322293498 | 0.155907752 |
| C | -0.0000051488 | 0.0000071119 | -0.2135368121 | C | 2.7274274542 | 3.2058047607 | -1.0981960963 |
| C | 2.458345611 | -0.2471081106 | 0.0456339883 | C | 3.41696697 | 2.9782738324 | 1.3334726056 |
| C | 2.9463591403 | -1.5453326809 | -0.2019852563 | C | 2.1112473917 | -2.8041894436 | -0.0226781574 |
| C | 3.2192026898 | 0.9266697691 | -0.123033828 | C | 2.7393425505 | -3.7625502491 | 0.998135402 |
| C | 4.2714587001 | -1.6416705086 | -0.6442643101 | C | 1.8604513479 | -3.4993595815 | -1.3683855626 |
| C | 4.5369659931 | 0.7597161204 | -0.5656165382 | H | 1.3951886469 | -0.1424592264 | 2.6660127269 |
| C | 5.0570751054 | -0.5060133065 | -0.8234891034 | H | -1.395118132 | 0.1423502121 | 2.6660573181 |
| C | -2.4583481929 | 0.2471081152 | 0.0457137416 | H | 4.6963713728 | -2.6265300208 | -0.8523937308 |
| C | -2.9463674597 | 1.5453425647 | -0.2018394298 | H | 5.1682464823 | 1.6396491213 | -0.7116570612 |
| C | -3.219211038 | -0.9266623554 | -0.1229784443 | H | 6.0890149806 | -0.6087069884 | -1.1692029811 |
| C | -4.2714793853 | 1.6416995139 | -0.644077078 | H | -4.6963967695 | 2.6265675394 | -0.8521567021 |
| C | -4.5369869145 | -0.7596900596 | -0.5655169225 | H | -5.1682726168 | -1.6396165693 | -0.7115744313 |
| C | -5.0571022185 | 0.5060501478 | -0.8233243511 | H | -6.0890519126 | 0.6087586248 | -1.1690048942 |
| C | -2.6821041887 | -2.3222977803 | 0.1558938505 | H | -1.6226322751 | -2.231176418 | 0.4470337834 |
| C | -2.7274610312 | -3.2057585546 | -1.0982444885 | H | -2.1843502866 | -2.7484519943 | -1.9398109637 |
| C | -3.4169421211 | -2.9783253364 | 1.3334495383 | H | -2.2732855122 | -4.1874253695 | -0.8918004516 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -3.7618394279 | -3.3875356725 | -1.4293503402 | H | 2.27325612 | 4.1874629087 | -0.8917015774 |
| H | -3.3635127464 | -2.3622575528 | 2.2446739406 | H | 3.7617976459 | 3.3875960647 | -1.429319797 |
| H | -4.4822677196 | -3.1381871001 | 1.1043740697 | H | 3.3635567167 | 2.3621705916 | 2.244674264 |
| H | -2.977174615 | -3.9616920319 | 1.5621141309 | H | 4.4822877946 | 3.1381421629 | 1.1043794059 |
| H | -1.1276831906 | 2.509896428 | 0.3795661682 | H | 2.9772063888 | 3.9616324851 | 1.5621849872 |
| H | -2.9047314141 | 3.2732752248 | 1.9707130176 | H | 1.1276805134 | -2.5099104991 | 0.3794010772 |
| H | -2.0826112579 | 4.6311016997 | 1.1620578202 | H | 2.9047245904 | -3.2732805758 | 1.9705531106 |
| H | -3.7105102783 | 4.1478390524 | 0.6503186842 | H | 2.08263771 | -4.6311151397 | 1.1618771892 |
| H | -1.377910866 | 2.8252409622 | -2.0931837143 | H | 3.7105323823 | -4.1478139335 | 0.6501567448 |
| H | -2.8008824022 | 3.8523245108 | -1.819667802 | H | 1.3779261085 | -2.8252338932 | -2.093350232 |
| H | -1.2097946304 | 4.3774218454 | -1.232721669 | H | 2.8009014281 | -3.8523123084 | -1.8198324042 |
| H | 1.6226361385 | 2.2311594087 | 0.447069153 | H | 1.2098140958 | -4.3774200781 | -1.2328971061 |
| H | 2.1842964799 | 2.7485316522 | -1.9397677122 | | | | |

Coordinates of Optimized Structures of [FcH-*i*Pr]$^{+}$ Isomer 1 (IVa-1)

E° = -2808.9156037; G° = -2808.245985; E°$_{(THF)}$ = -2808.991924

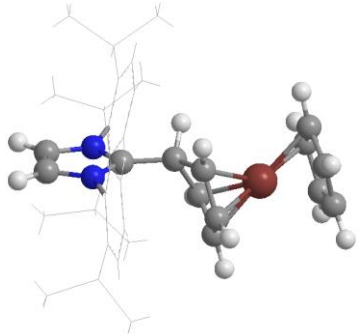


| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.6464494231 | 2.4915209497 | 0.6481665041 | C | 0.5903637665 | 1.5045932431 | -3.0910898884 |
| C | -4.6666087704 | 1.1229576406 | 1.0183859431 | C | 0.9674293112 | 2.6424208602 | -3.8146776964 |
| C | -4.1541335099 | 0.3547308403 | -0.0732273507 | C | 2.0261253727 | 3.4473704195 | -3.402672534 |
| C | -3.7873106594 | 1.2635812287 | -1.1071344588 | C | 2.7455096401 | 3.1220038268 | -2.2580852896 |
| C | -4.0729481624 | 2.585295165 | -0.6453556552 | C | 2.4254677689 | 1.9915394948 | -1.4952247964 |
| Fe | -2.6286631182 | 1.6095798102 | 0.5949023582 | C | 3.2942124847 | 1.637113281 | -0.297603481 |
| C | 1.5399148697 | -1.215285102 | -1.5680311419 | C | 4.6806677814 | 1.1593289002 | -0.755133584 |
| C | 1.1959744494 | -2.1187280288 | -0.6179830324 | C | 3.4062919296 | 2.7940270297 | 0.7033513326 |
| N | 0.4650081013 | -1.4458306739 | 0.3433667535 | C | -0.5484588641 | 0.629927309 | -3.5972047636 |
| C | 0.358414352 | -0.1380684402 | -0.0042348297 | C | -1.7116841226 | 1.4503081865 | -4.1671742432 |
| N | 1.0178519822 | 0.005122038 | -1.181949254 | C | -0.0566796179 | -0.3738147603 | -4.6531289339 |
| C | 1.3287533434 | 1.2139168351 | -1.922955042 | C | 2.218008622 | -1.1971135285 | 2.6845438651 |
| C | -1.347007652 | 2.9647584349 | 1.3073010345 | C | 3.4278323883 | -2.1425556437 | 2.7297474978 |
| C | -1.6983344289 | 2.0202949207 | 2.3137362674 | C | 2.2791750347 | -0.1596258562 | 3.812781128 |
| C | -1.2896720669 | 0.731337635 | 1.8447920877 | C | -1.9597113976 | -3.1224399868 | 0.3383496277 |
| C | -0.1278277943 | 0.9750876868 | 0.8732794433 | C | -1.5435880033 | -4.3757545898 | -0.4498506634 |
| C | -0.7308016075 | 2.2357767215 | 0.2407985022 | C | -3.451058936 | -3.2068191771 | 0.68492808 |
| C | 0.0695588483 | -2.1084691245 | 1.5731049286 | H | -4.9585376128 | 3.3289978441 | 1.2723324075 |
| C | -1.0834099183 | -2.9242317818 | 1.5677165127 | H | -5.0273459087 | 0.7247307695 | 1.9669453208 |
| C | -1.3910460488 | -3.5970460328 | 2.7565601543 | H | -4.1014136572 | -0.7301465643 | -0.11668807 |
| C | -0.5928079741 | -3.4711820839 | 3.8903587693 | H | -3.3963855179 | 1.0039497327 | -2.0878179957 |
| C | 0.5484158115 | -2.6776414622 | 3.8553951911 | H | -3.8930559083 | 3.5083620563 | -1.1967872018 |
| C | 0.9175116987 | -1.9864588366 | 2.6942049528 | H | 2.125071049 | -1.3196677476 | -2.4765229793 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 1.4185838009 | -3.17701726 | -0.5224428907 | H | -2.5771793014 | 0.7979739609 | -4.3619765979 |
| H | -1.5745473901 | 4.0315501354 | 1.3125184178 | H | -2.0265703062 | 2.2503636282 | -3.4810993293 |
| H | -2.2458964603 | 2.2279223842 | 3.2340709168 | H | -1.450619899 | 1.9171970892 | -5.1294105328 |
| H | -1.400735398 | -0.1750275309 | 2.4389516974 | H | -0.8878521768 | -1.0094299923 | -4.9970808343 |
| H | 0.7976695925 | 1.2383739103 | 1.4442587434 | H | 0.7334170739 | -1.0379326692 | -4.2738791945 |
| H | -0.3263817002 | 2.7202439204 | -0.6472520493 | H | 0.3482123021 | 0.152776607 | -5.5319456558 |
| H | -2.2755673158 | -4.2354362251 | 2.7975672376 | H | 2.2788121057 | -0.64655677 | 1.7328397672 |
| H | -0.8591696848 | -4.005088389 | 4.8063383038 | H | 4.3676902551 | -1.5717006282 | 2.6666977627 |
| H | 1.1768722173 | -2.6015481497 | 4.7459053193 | H | 3.451035472 | -2.7179980241 | 3.6686502418 |
| H | 0.4218951381 | 2.9061562244 | -4.7228380137 | H | 3.4133102054 | -2.8651609838 | 1.8990777136 |
| H | 2.297217731 | 4.3317300467 | -3.9852818627 | H | 2.3044465238 | -0.6371264166 | 4.8046925127 |
| H | 3.5845620635 | 3.7527265864 | -1.9548326327 | H | 1.4130998457 | 0.5199331965 | 3.7935005268 |
| H | 2.8241031159 | 0.7933519733 | 0.23157393 | H | 3.1928695447 | 0.4486057746 | 3.7246886343 |
| H | 5.2901618953 | 0.8544321906 | 0.1101166684 | H | -1.8197877582 | -2.2447658927 | -0.3151201905 |
| H | 4.6118276955 | 0.3007247557 | -1.4410335374 | H | -0.4988622533 | -4.3377181331 | -0.7898525894 |
| H | 5.2256847409 | 1.9596044656 | -1.2803834343 | H | -1.6567484762 | -5.2799642616 | 0.1691284235 |
| H | 3.9647559772 | 2.4747335246 | 1.5971044179 | H | -2.1786792164 | -4.4979533447 | -1.3413288408 |
| H | 2.4174790108 | 3.1532961118 | 1.0279506942 | H | -4.0572031569 | -3.164986296 | -0.2334016654 |
| H | 3.9472104935 | 3.6524963387 | 0.2755020351 | H | -3.7676320634 | -2.3892079043 | 1.349081064 |
| H | -0.937330053 | 0.05930651 | -2.7371897573 | H | -3.702739116 | -4.156649902 | 1.1816198033 |

Coordinates of Optimized Structures of [FcH-*i*Pr]$^{+}$ Isomer 2 (IVa-2)
: More stable than IVa-1 (-9.8 kcal/mol)

E° = -2808.9292187; G° = -2808.261599; E°$_{(THF)}$ = -2809.0049039



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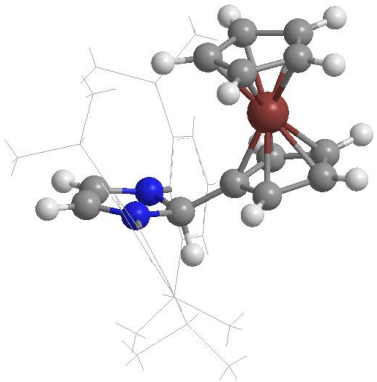
|---|---|---|---|---|---|---|---|
| C | -4.4972774547 | 2.5399149634 | 1.5671885315 | C | -0.5762081465 | 2.2282326184 | 0.9937982541 |
| C | -4.616482751 | 1.2729885107 | 0.9417581002 | C | 1.0884864609 | -1.3694611634 | 2.465021762 |
| C | -4.0615021743 | 1.365196346 | -0.3741586553 | C | 0.564579689 | -2.6183806785 | 2.072722762 |
| C | -3.5673543678 | 2.6920105208 | -0.5426082677 | C | -0.0022360665 | -3.4133448716 | 3.0764051483 |
| C | -3.8206423359 | 3.4060877012 | 0.6711025115 | C | -0.0298698521 | -2.9888955007 | 4.4020315545 |
| Fe | -2.5308128794 | 1.7327633009 | 0.9851577298 | C | 0.5204316375 | -1.7603080184 | 4.7582821177 |
| C | 3.3717784755 | 0.1951644709 | 0.1758100879 | C | 1.1003837634 | -0.9185611828 | 3.8012791653 |
| C | 3.0855659565 | -0.6694310675 | 1.183477148 | C | 1.6816016875 | 1.3949114981 | -2.4867476493 |
| N | 1.7340969724 | -0.5512304472 | 1.4570365283 | C | 1.6027618304 | 2.3724035676 | -3.4866986349 |
| C | 1.1903917466 | 0.3659991497 | 0.6275900063 | C | 1.9172144911 | 3.7020590306 | -3.2214069795 |
| N | 2.1921362072 | 0.831349646 | -0.1538554926 | C | 2.3282313351 | 4.0864195385 | -1.9475549324 |
| C | 2.0788722422 | 1.821976423 | -1.2023606262 | C | 2.423901702 | 3.1581958244 | -0.903617859 |
| C | -1.0946508062 | 2.1274044901 | 2.323907976 | C | 2.9436873225 | 3.5930323997 | 0.4601730453 |
| C | -1.5862110193 | 0.7987305488 | 2.481821087 | C | 4.4777836612 | 3.6962664404 | 0.4456966972 |
| C | -1.3501897481 | 0.1111988714 | 1.2492230622 | C | 2.3278821424 | 4.9091252638 | 0.949283951 |
| C | -0.2495054139 | 0.8231106226 | 0.4751642239 | C | 1.4001642697 | -0.0620033047 | -2.8269944913 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.0644490045 | -0.2519155284 | -3.5559027748 | H | 4.8578064638 | 3.9646178364 | 1.4440143385 |
| C | 2.5622802941 | -0.6615578368 | -3.6339785156 | H | 4.9583001962 | 2.7527778212 | 0.1457419248 |
| C | 1.7643390585 | 0.3842691371 | 4.2267164579 | H | 4.8113615763 | 4.4731145139 | -0.2605202558 |
| C | 3.2016250515 | 0.1277945377 | 4.7101008774 | H | 2.6469635794 | 5.1135368752 | 1.982971311 |
| C | 0.9761538525 | 1.1437358979 | 5.2991004945 | H | 1.2279463645 | 4.883879644 | 0.935175513 |
| C | 0.6517538243 | -3.1407525747 | 0.6449363433 | H | 2.6514319744 | 5.7668191142 | 0.3393273435 |
| C | 1.8106661909 | -4.1414207908 | 0.5083313783 | H | 1.3379067986 | -0.6281759003 | -1.8832941393 |
| C | -0.6592149413 | -3.7609021617 | 0.1481702259 | H | -0.142273799 | -1.3238347494 | -3.6997684246 |
| H | -4.815326495 | 2.7867220221 | 2.5801596407 | H | -0.7770584921 | 0.1832099695 | -2.9942509824 |
| H | -5.068416329 | 0.3837174993 | 1.3815706501 | H | 0.0722481803 | 0.2114096584 | -4.5545650879 |
| H | -4.0483269498 | 0.5665263232 | -1.11546091 | H | 2.3823393098 | -1.728643042 | -3.8392516619 |
| H | -3.1015738146 | 3.1046056691 | -1.4373962129 | H | 3.5199248526 | -0.5764265208 | -3.0972982989 |
| H | -3.5523911136 | 4.4445023303 | 0.8666025631 | H | 2.6795037224 | -0.1499476255 | -4.6024485292 |
| H | 4.3022080338 | 0.4104502279 | -0.3414140524 | H | 1.8183468474 | 1.0379837147 | 3.3403970145 |
| H | 3.7153639028 | -1.3651962324 | 1.7298408927 | H | 3.6921523207 | 1.0748416654 | 4.9854069016 |
| H | -1.1769379281 | 2.938417876 | 3.0486897228 | H | 3.2049682895 | -0.5227077459 | 5.5991796884 |
| H | -2.1083606002 | 0.3983388208 | 3.3513286727 | H | 3.8221452569 | -0.3597021525 | 3.9434502525 |
| H | -1.6309487667 | -0.9269027328 | 1.0727564168 | H | 0.9874653877 | 0.6191322293 | 6.2672635503 |
| H | -0.429459995 | 0.7737299858 | -0.6121926988 | H | -0.0730601279 | 1.2955230163 | 5.0076385926 |
| H | -0.1378991562 | 3.1300960845 | 0.5661216308 | H | 1.4290442709 | 2.1328668846 | 5.4686432239 |
| H | -0.4226949843 | -4.3875176808 | 2.8168020734 | H | 0.8756817624 | -2.2871484224 | -0.0159388902 |
| H | -0.4758625382 | -3.6279958401 | 5.1687365116 | H | 2.7750557022 | -3.6998225689 | 0.8026319116 |
| H | 0.5040852525 | -1.4506941082 | 5.8052990517 | H | 1.6442028399 | -5.0247917878 | 1.1450655031 |
| H | 1.2985483295 | 2.0846084003 | -4.4957983991 | H | 1.9026792463 | -4.4903559165 | -0.5324094775 |
| H | 1.8508634898 | 4.4466069415 | -4.019134653 | H | -0.5747424381 | -4.021060587 | -0.91839105 |
| H | 2.5862133485 | 5.1313329294 | -1.7616991783 | H | -1.5124446974 | -3.0747061834 | 0.2612914683 |
| H | 2.6679326514 | 2.8142804249 | 1.1901748804 | H | -0.9051536374 | -4.6902878739 | 0.6848903089 |

Coordinates of Optimized Structures of [Fc-*i*Pr-H]$^+$ Isomer 1 (Va-1)

E° = -2808.8998339; G° = -2808.228478; E°$_{(THF)}$ = -2808.9777557



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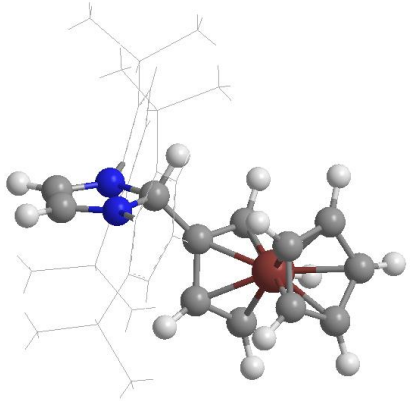
|---|---|---|---|---|---|---|---|
| C | -4.5372283314 | 2.1677037755 | 1.8696661923 | C | -0.1760238634 | -0.0395630913 | -0.1683083645 |
| C | -4.388989164 | 0.7886231965 | 1.5388601257 | N | -0.0970597037 | -0.0143154947 | -1.6452868718 |
| C | -4.2478424021 | 0.6904456037 | 0.121327642 | C | 0.4876762702 | 1.0373939486 | -2.4471259655 |
| C | -4.307059578 | 2.0084440438 | -0.4201065886 | C | -1.3195674125 | 3.2888726275 | 1.1237952031 |
| C | -4.4838038871 | 2.920924488 | 0.6602479266 | C | -1.4051442815 | 2.4964635714 | 2.3036367523 |
| Fe | -2.7572403696 | 1.8503773719 | 0.9190243371 | C | -1.1474435104 | 1.1412237719 | 1.9502427227 |
| C | -0.2842131342 | -1.2612832142 | -2.1209761194 | C | -0.9035262203 | 1.0846528336 | 0.5324691578 |
| C | -0.5773357011 | -2.1197919673 | -1.0816895631 | C | -1.0082994326 | 2.43022949 | 0.032226407 |
| N | -0.5815196659 | -1.4466341313 | 0.0897811734 | C | -0.8923303942 | -2.0757273341 | 1.3468399494 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.1047066458 | -2.8131313566 | 1.4547924521 | H | -3.322724676 | -3.9708288555 | 2.8030667912 |
| C | -2.3954220635 | -3.405480826 | 2.691657329 | H | -1.7967153919 | -3.7542828389 | 4.7327131589 |
| C | -1.5387645745 | -3.29173309 | 3.7766033405 | H | 0.3485580234 | -2.5621792321 | 4.4825395251 |
| C | -0.3344018888 | -2.60830404 | 3.6341438474 | H | -0.3616942597 | 3.2867351876 | -4.8530024374 |
| C | 0.0328021511 | -2.0066576554 | 2.4268884098 | H | 2.0351076804 | 3.8442711562 | -4.620722812 |
| C | -0.3423149952 | 1.7298670113 | -3.3620715349 | H | 3.4653477257 | 2.559545397 | -3.0655395236 |
| C | 0.2497163708 | 2.7335551708 | -4.1374096885 | H | 2.2782793773 | -0.3704541669 | -1.0590711643 |
| C | 1.6002732976 | 3.0462739005 | -4.0133182232 | H | 4.5977702072 | -0.7673123008 | -1.6617274902 |
| C | 2.3996371902 | 2.3276582934 | -3.1321795107 | H | 3.605128864 | -0.7115903301 | -3.1402446709 |
| C | 1.8747244214 | 1.2930118963 | -2.3469449974 | H | 4.6421237442 | 0.6647959521 | -2.7050150258 |
| C | 2.8291930488 | 0.4882808663 | -1.4744940035 | H | 4.0143163004 | 0.720316076 | 0.3462024963 |
| C | 3.9791992037 | -0.112763864 | -2.2956128561 | H | 2.547363213 | 1.7386554177 | 0.3165985228 |
| C | 3.3603161439 | 1.3250255725 | -0.3016035781 | H | 3.9549259755 | 2.1784896105 | -0.6636319805 |
| C | -1.8158593189 | 1.3997899521 | -3.561354515 | H | -2.1632373891 | 0.8715229663 | -2.6580974413 |
| C | -2.6888817222 | 2.6496024231 | -3.7233015887 | H | -3.7523480039 | 2.3658255007 | -3.7550817661 |
| C | -2.0124161166 | 0.4683898738 | -4.7692104817 | H | -2.547624014 | 3.3628690615 | -2.8973714957 |
| C | 1.4346393753 | -1.4153318898 | 2.2969884077 | H | -2.4807982826 | 3.1804511893 | -4.6650724067 |
| C | 2.3329171861 | -2.3564455859 | 1.4770545567 | H | -3.0741874055 | 0.1980356926 | -4.8825001291 |
| C | 2.103233807 | -1.0769274158 | 3.6320797761 | H | -1.4368753399 | -0.4658897819 | -4.6854078637 |
| C | -3.0838129032 | -3.071889914 | 0.3123389386 | H | -1.6916155229 | 0.9624234675 | -5.7001747757 |
| C | -2.8842229028 | -4.487624839 | -0.2603303648 | H | 1.3633883218 | -0.4549943814 | 1.7643728821 |
| C | -4.5553132258 | -2.9032964377 | 0.7148121931 | H | 3.3383629456 | -1.9246892743 | 1.35302095 |
| H | -4.6497575154 | 2.5757122381 | 2.8738694638 | H | 2.4458819058 | -3.3240208962 | 1.9910240503 |
| H | -4.3700298899 | -0.0331589629 | 2.2535010099 | H | 1.9281215106 | -2.562901295 | 0.4742076663 |
| H | -4.1228691213 | -0.2258625538 | -0.4525807015 | H | 2.3603164075 | -1.9777633913 | 4.2106608256 |
| H | -4.2308918327 | 2.2743194202 | -1.4717479042 | H | 1.4706267314 | -0.4313791083 | 4.2602259867 |
| H | -4.5505847059 | 4.0054759014 | 0.5784713046 | H | 3.0451707042 | -0.5391669339 | 3.4455177722 |
| H | -0.1617608692 | -1.4968644152 | -3.1758649982 | H | -2.8887706455 | -2.340969935 | -0.4884408801 |
| H | -0.7512828255 | -3.1908820535 | -1.1296911385 | H | -1.8445118284 | -4.7029289197 | -0.5542947691 |
| H | 0.8723306594 | 0.0558581222 | 0.1765217311 | H | -3.1555545643 | -5.2470814124 | 0.4896795018 |
| H | -1.4902137786 | 4.3628325333 | 1.0564032312 | H | -3.5272672658 | -4.6450222414 | -1.1405355427 |
| H | -1.65774828 | 2.8537404212 | 3.3014110643 | H | -5.1961789282 | -2.9600162167 | -0.1786906928 |
| H | -1.1523058668 | 0.2989229795 | 2.6388675954 | H | -4.7473072192 | -1.9412863248 | 1.2067454218 |
| H | -0.8623894066 | 2.7475367685 | -0.9969339426 | H | -4.8901255253 | -3.7018377733 | 1.3942345761 |

Coordinates of Optimized Structures of **[**Fc-*i*Pr-H]$^{+}$ Isomer 2 (Va-2)

: More stable than Va-1 (-12.5 kcal/mol)

E° = -2808.9185591; G° = -2808.248363; E°$_{(THF)}$ = -2808.9966655



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.3024818865 | 4.1947270942 | 1.9842109861 | C | 1.4682234243 | 3.8776658846 | 0.6041431062 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 2.286533706 | 2.7137537269 | 0.5145063124 | H | 2.077562379 | 3.1847642534 | 3.8351484893 |
| C | 2.6287350127 | 2.3108704436 | 1.8396833658 | H | -1.1632539685 | -0.5914229208 | -3.3509007691 |
| C | 2.0202672226 | 3.2269987327 | 2.7476600859 | H | -2.4602788541 | -2.2993795353 | -1.6435289061 |
| Fe | 0.5920708813 | 2.3127868151 | 1.6064717156 | H | 0.8194024514 | -0.8191238715 | 0.1013202582 |
| C | -1.0388813901 | -0.6990990604 | -2.2755408972 | H | -0.6310354765 | 1.7250391355 | 4.0702667039 |
| C | -1.6848261196 | -1.5704723139 | -1.415108083 | H | -1.933569067 | 3.3379862812 | 2.32709888 |
| N | -1.1891708179 | -1.4219480687 | -0.1762874121 | H | -1.6472158385 | 2.3144341873 | -0.1473698027 |
| C | -0.1486817117 | -0.3540295733 | -0.1627682679 | H | 0.4860739567 | -0.2962195348 | 2.6685477862 |
| N | -0.1313204806 | 0.0281258185 | -1.5904962085 | H | -4.1774023633 | -2.4392940193 | 3.1799688818 |
| C | 0.8315333017 | 0.8876851798 | -2.2288711687 | H | -2.7181635711 | -4.2308724648 | 4.0555095605 |
| C | -0.7099646459 | 1.5750318082 | 2.9940788961 | H | -0.5794334054 | -4.7613657853 | 2.9321923706 |
| C | -1.3966358887 | 2.4238512071 | 2.0756493212 | H | 1.0620238894 | 3.8817647707 | -3.8255395976 |
| C | -1.2365654172 | 1.889339793 | 0.7651745674 | H | 3.4416630319 | 3.21485999 | -3.8932140739 |
| C | -0.4335102466 | 0.7060269515 | 0.8664446781 | H | 4.1383103843 | 1.0046768692 | -3.0259674927 |
| C | -0.107869023 | 0.5183642841 | 2.2549920123 | H | 1.7551217696 | -1.5149873327 | -1.5890100058 |
| C | -1.6063486842 | -2.1780260778 | 0.9729079126 | H | 3.4750608605 | -2.7484511822 | -2.8007999227 |
| C | -2.850269616 | -1.8774899129 | 1.5759613556 | H | 2.5222035609 | -1.771466244 | -3.9462059459 |
| C | -3.2232518972 | -2.6418164101 | 2.688143945 | H | 4.1558826638 | -1.2557201659 | -3.4736633706 |
| C | -2.4047964672 | -3.6533746534 | 3.181790635 | H | 3.9227632598 | -1.9000296447 | -0.4365848532 |
| C | -1.1975652175 | -3.9436730439 | 2.5533826828 | H | 3.1945609233 | -0.3761786126 | 0.1330386516 |
| C | -0.7736976862 | -3.2248506289 | 1.4296764201 | H | 4.5418639594 | -0.3429353092 | -1.0200773626 |
| C | 0.3936141139 | 2.1092838947 | -2.7956593788 | H | -1.6539716585 | 1.8587205417 | -2.227506875 |
| C | 1.3644880517 | 2.928538392 | -3.3856428165 | H | -2.4016662288 | 4.1805526885 | -2.4215824551 |
| C | 2.703073294 | 2.5513700267 | -3.4359540209 | H | -0.9533117792 | 4.1276087508 | -1.3874596709 |
| C | 3.0937502203 | 1.3129656588 | -2.9359411996 | H | -0.8387064331 | 4.7007130952 | -3.0669484077 |
| C | 2.1701572668 | 0.4435085883 | -2.3428235689 | H | -2.6698201663 | 2.5663101609 | -4.3686072309 |
| C | 2.6370869207 | -0.9424656393 | -1.9168338819 | H | -1.4507043404 | 1.3055952698 | -4.6825454779 |
| C | 3.2281482793 | -1.7185627802 | -3.1031326194 | H | -1.0731295665 | 3.0018771211 | -5.0187428832 |
| C | 3.6242470284 | -0.8857573353 | -0.7437235292 | H | 0.7021591232 | -2.9262701991 | -0.0910693294 |
| C | -1.0697259722 | 2.5245597536 | -2.8817962711 | H | 1.1960746751 | -5.2981716064 | -0.5447233759 |
| C | -1.322571341 | 3.9614384757 | -2.4100283838 | H | 0.1034948804 | -5.809071495 | 0.7611151189 |
| C | -1.5944829865 | 2.3338950359 | -4.3150707581 | H | -0.5555261277 | -4.995476072 | -0.6727046586 |
| C | 0.49776256 | -3.6536659228 | 0.7104289541 | H | 1.609307142 | -4.4173427967 | 2.4401452228 |
| C | 0.2967786279 | -5.0136678197 | 0.0242952901 | H | 1.889930515 | -2.6950633653 | 2.1141895404 |
| C | 1.719565665 | -3.6727407692 | 1.6366475387 | H | 2.6270706998 | -3.9386586709 | 1.0725745272 |
| C | -3.8010517866 | -0.8152734993 | 1.0435744599 | H | -3.2398817355 | -0.1824493404 | 0.3386008473 |
| C | -4.9644191175 | -1.4613363239 | 0.2736054825 | H | -4.6186016904 | -2.1074841028 | -0.5486732519 |
| C | -4.3307012666 | 0.1094107986 | 2.1454340585 | H | -5.579799401 | -2.087448559 | 0.9391946086 |
| H | 0.7171187763 | 5.0209388873 | 2.3870628565 | H | -5.620580509 | -0.6886977895 | -0.1574311845 |
| H | 1.0429108371 | 4.4257634739 | -0.2346780584 | H | -4.9182785691 | 0.9280892152 | 1.7013259904 |
| H | 2.5833539621 | 2.2171871382 | -0.4062411777 | H | -3.5107328845 | 0.5548542956 | 2.7266252747 |
| H | 3.2431601562 | 1.4547508296 | 2.1173082011 | H | -4.9966679061 | -0.4217518651 | 2.843311054 |

Coordinates of Optimized Structures of **[**Fc-*i*Pr] radical (**3a**)

E° = -2808.5019729; G° = -2807.849952; $E°_{(THF)}$ = -2808.533353

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.4676037375 | 1.9888374517 | 1.3075813086 | Fe | -2.4831927208 | 1.7352910321 | 0.7235780224 |
| C | -4.2226925596 | 0.6393007621 | 0.903237657 | C | 1.521839219 | -1.2658687002 | -1.5649616553 |
| C | -3.8036012244 | 0.6504297389 | -0.4611499112 | C | 1.2105195349 | -2.1244871431 | -0.573347326 |
| C | -3.7529697013 | 2.0116019891 | -0.8849254931 | N | 0.4520394943 | -1.4456120268 | 0.3770443319 |
| C | -4.1751637762 | 2.8365323975 | 0.2041055284 | C | 0.2911896461 | -0.105524496 | -0.029404526 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N | 0.9612283061 | -0.0263409613 | -1.267031524 | H | -1.8055621929 | 2.4749654088 | 3.3158948499 |
| C | 1.3325986265 | 1.1448067671 | -2.0008427451 | H | -1.2083922007 | -0.0175214584 | 2.5354022699 |
| C | -1.0836305196 | 3.0837607589 | 1.2729422139 | H | -0.2719037102 | 2.7066659354 | -0.7706331618 |
| C | -1.3841950355 | 2.198815391 | 2.3491537531 | H | -2.2283862406 | -4.4152463271 | 2.6485853875 |
| C | -1.0726058119 | 0.8714240761 | 1.9256951013 | H | -1.0862256635 | -3.9531942052 | 4.796135465 |
| C | -0.3929051917 | 0.9270042737 | 0.636628977 | H | 0.7735535342 | -2.3224059804 | 4.8911879819 |
| C | -0.5857478025 | 2.3014883425 | 0.1878191771 | H | 0.5001091755 | 2.8502814907 | -4.8303315231 |
| C | 0.0173935054 | -2.0866627066 | 1.5775534512 | H | 2.4249986359 | 4.2190162022 | -4.0976859038 |
| C | -1.0397784857 | -3.0219441525 | 1.5042916106 | H | 3.6644652399 | 3.6275995684 | -2.0368444067 |
| C | -1.4135087066 | -3.6869791398 | 2.6801589065 | H | 2.7675931402 | 0.6796071028 | 0.1290978958 |
| C | -0.7733192451 | -3.4302319025 | 3.8879409773 | H | 5.2377277665 | 0.8058055061 | 0.176062429 |
| C | 0.2709006307 | -2.508333135 | 3.939360503 | H | 4.6752139293 | 0.2835569698 | -1.4312039251 |
| C | 0.6974071904 | -1.8303441102 | 2.7925799255 | H | 5.2386266806 | 1.9520268132 | -1.1831839979 |
| C | 0.6157013113 | 1.4659396415 | -3.1764363982 | H | 3.7989304948 | 2.3663707101 | 1.6013509031 |
| C | 1.034830744 | 2.5777951918 | -3.9173698307 | H | 2.233587524 | 2.9556155388 | 0.9866228036 |
| C | 2.1183773998 | 3.3509384221 | -3.5071192518 | H | 3.7582677644 | 3.582494751 | 0.3086962716 |
| C | 2.81139544 | 3.0177305288 | -2.3472257299 | H | -0.9587727239 | 0.1099008383 | -2.7559137615 |
| C | 2.4426747247 | 1.9077317612 | -1.5763444738 | H | -2.6055995731 | 0.8674220368 | -4.3668018817 |
| C | 3.2524472723 | 1.5472845364 | -0.3414752565 | H | -1.9710249343 | 2.3125613126 | -3.5417578901 |
| C | 4.678622637 | 1.1235723236 | -0.7190136199 | H | -1.445790648 | 1.9175766461 | -5.1955907263 |
| C | 3.2574801649 | 2.6788539481 | 0.6936838307 | H | -1.0032938129 | -1.0382881934 | -4.9802021793 |
| C | -0.5687084141 | 0.6328310462 | -3.6434660808 | H | 0.6185807862 | -1.1153597303 | -4.2586856266 |
| C | -1.7060876815 | 1.4848782384 | -4.2159494421 | H | 0.2855107704 | 0.0417896601 | -5.5675398708 |
| C | -0.1391236304 | -0.4303241344 | -4.6660640908 | H | 1.7906737192 | -0.1754011737 | 2.0261293337 |
| C | 1.8971446154 | -0.8967665836 | 2.8506386709 | H | 4.0668375561 | -1.007671391 | 2.6170505323 |
| C | 3.1961029813 | -1.6837480741 | 2.6161745809 | H | 3.3512414835 | -2.4343067899 | 3.4089363199 |
| C | 1.9765156197 | -0.0826850668 | 4.1447266789 | H | 3.1827950677 | -2.2130376838 | 1.651106269 |
| C | -1.7598413874 | -3.3403794886 | 0.2017942605 | H | 2.1941032183 | -0.7124741817 | 5.0229124444 |
| C | -1.3720277402 | -4.7304570936 | -0.3235128399 | H | 1.0400523439 | 0.4628752235 | 4.3358006432 |
| C | -3.2822162587 | -3.2192714249 | 0.3334558519 | H | 2.787933877 | 0.658850787 | 4.0739916242 |
| H | -4.8014766403 | 2.3091160555 | 2.2945527396 | H | -1.4357587794 | -2.5975274652 | -0.542758817 |
| H | -4.3529047153 | -0.2408487488 | 1.5325100514 | H | -0.2857668068 | -4.8278465338 | -0.4719863098 |
| H | -3.5514708511 | -0.2201701344 | -1.0664006882 | H | -1.6806852984 | -5.5213859379 | 0.3797961319 |
| H | -3.4674353776 | 2.3643921025 | -1.8744828247 | H | -1.8625098045 | -4.9324808287 | -1.2897317124 |
| H | -4.2460445154 | 3.924196042 | 0.1920221542 | H | -3.7641675056 | -3.3505500507 | -0.6486915814 |
| H | 2.121116047 | -1.4108035555 | -2.4586650603 | H | -3.5720944345 | -2.2337826667 | 0.7237636819 |
| H | 1.4679172303 | -3.1709260165 | -0.4407709857 | H | -3.7006063373 | -3.9860480268 | 1.0054196302 |
| H | -1.2314186514 | 4.1637270995 | 1.2622878971 | | | | |

Coordinates of Optimized Structures of [Fc-*i*Pr]$^{+}$ (VIIa)

E° = -2808.3679658; G° = -2807.707831; E°$_{(THF)}$ = -2808.443071

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.2417166264 | 1.8812481638 | 1.454015317 | C | 0.2880519445 | -0.0922760269 | -0.0462934154 |
| C | -3.9876905133 | 0.5364132221 | 1.0540798842 | N | 1.0339888124 | -0.0021341577 | -1.1835841826 |
| C | -3.6452644744 | 0.5495087264 | -0.3313800127 | C | 1.3362007862 | 1.1578492369 | -1.9942810298 |
| C | -3.6851439326 | 1.9003893783 | -0.7853041291 | C | -0.9901630456 | 3.1881573134 | 1.1622408839 |
| C | -4.0528500676 | 2.7234543009 | 0.319110781 | C | -1.2025064494 | 2.3749361288 | 2.3123712399 |
| Fe | -2.3329326615 | 1.7022841401 | 0.748942694 | C | -0.8653770084 | 1.034876581 | 1.9848144784 |
| C | 1.6403057024 | -1.2164871593 | -1.43821368 | C | -0.388487602 | 1.0116226765 | 0.6170206809 |
| C | 1.2668679758 | -2.0675288902 | -0.4525426948 | C | -0.5157097376 | 2.3622425231 | 0.1090959754 |
| N | 0.4281497314 | -1.3740346222 | 0.3986065733 | C | -0.1124427201 | -2.0048633158 | 1.5849498557 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.2551095504 | -2.8232953253 | 1.4526017616 | H | -1.4739193972 | -3.7761810584 | 4.7306970597 |
| C | -1.7282816463 | -3.4456062948 | 2.6155539439 | H | 0.5801756244 | -2.4078218578 | 4.8849639594 |
| C | -1.0836506712 | -3.2800752121 | 3.8380992523 | H | 0.4037050001 | 2.6738517989 | -4.8845335305 |
| C | 0.0691969994 | -2.5036683431 | 3.924491561 | H | 2.2681287381 | 4.1575330654 | -4.2319309688 |
| C | 0.5926471484 | -1.8552466952 | 2.7996211568 | H | 3.5585475369 | 3.7170502095 | -2.1690315397 |
| C | 0.5913925349 | 1.3709954231 | -3.1738900213 | H | 2.7896178554 | 0.8900091547 | 0.1994216842 |
| C | 0.9531210703 | 2.4696237734 | -3.9631826433 | H | 5.2602585176 | 1.0069638246 | 0.1486977802 |
| C | 2.0055764432 | 3.3062645789 | -3.5982650754 | H | 4.6471208049 | 0.3437723834 | -1.3864631123 |
| C | 2.72888301 | 3.0578171137 | -2.4356350676 | H | 5.2140334704 | 2.0250762058 | -1.3068132433 |
| C | 2.4189098339 | 1.9732808045 | -1.6053675396 | H | 3.8659578041 | 2.6760522611 | 1.4878862863 |
| C | 3.2604233729 | 1.7102219125 | -0.3652852839 | H | 2.3032431445 | 3.2563211541 | 0.8605203954 |
| C | 4.6716617615 | 1.2432434153 | -0.7517661405 | H | 3.8266487576 | 3.7792217642 | 0.1024356115 |
| C | 3.3115599745 | 2.9252199277 | 0.5695462927 | H | -0.8916751234 | -0.0902780687 | -2.7179177822 |
| C | -0.5329904785 | 0.4438184836 | -3.6136954466 | H | -2.5804157299 | 0.5141715457 | -4.3429473746 |
| C | -1.7298893493 | 1.1989987267 | -4.2023609092 | H | -2.0560785038 | 2.0223418571 | -3.5497279978 |
| C | -0.0233416074 | -0.6060512289 | -4.6140395405 | H | -1.5001119827 | 1.6273455697 | -5.1903370788 |
| C | 1.9044500453 | -1.0889047751 | 2.9026472313 | H | -0.8370579115 | -1.2876046588 | -4.9082155321 |
| C | 3.0913455199 | -2.0650496298 | 2.8518975398 | H | 0.7921715733 | -1.2177946406 | -4.2006360876 |
| C | 1.9910036254 | -0.1933145336 | 4.1431003435 | H | 0.3564325021 | -0.122459203 | -5.5280799014 |
| C | -1.9136829219 | -3.1170886111 | 0.1107033133 | H | 1.9818983045 | -0.4290424798 | 2.0237515833 |
| C | -1.3795016445 | -4.4359821222 | -0.4749944962 | H | 4.0461446614 | -1.5167024907 | 2.8813501777 |
| C | -3.4437455013 | -3.1736677553 | 0.1785200729 | H | 3.0721050963 | -2.751988027 | 3.7129381667 |
| H | -4.5120557554 | 2.2107241534 | 2.4569351699 | H | 3.083332396 | -2.6799091747 | 1.9387640447 |
| H | -4.0351343269 | -0.3366583155 | 1.703218519 | H | 2.0273357354 | -0.7794302166 | 5.0745376331 |
| H | -3.3907490132 | -0.3183356561 | -0.9384773384 | H | 1.1400673523 | 0.5008084338 | 4.2107840462 |
| H | -3.4710760326 | 2.2456433599 | -1.7950728275 | H | 2.9124664988 | 0.4082148128 | 4.1091809163 |
| H | -4.154954464 | 3.8082780814 | 0.3038875047 | H | -1.6406284619 | -2.3037090431 | -0.5824919538 |
| H | 2.2984489148 | -1.3516692826 | -2.2911891054 | H | -0.2872075366 | -4.435454407 | -0.6002362705 |
| H | 1.5278342022 | -3.104433307 | -0.2663091398 | H | -1.6339367818 | -5.2831485241 | 0.1814635584 |
| H | -1.1882882141 | 4.2566261397 | 1.0857111007 | H | -1.82920374 | -4.6294881518 | -1.4615736632 |
| H | -1.5914878899 | 2.7106041861 | 3.273083071 | H | -3.8635343518 | -3.2499012744 | -0.8364218383 |
| H | -0.9343813277 | 0.1859675881 | 2.6588434654 | H | -3.8754786399 | -2.2844955835 | 0.6574456112 |
| H | -0.2716291914 | 2.7029367247 | -0.8925431515 | H | -3.7964972484 | -4.0574867305 | 0.7323286625 |
| H | -2.6133969495 | -4.0826929749 | 2.5601949057 | | | | |

Coordinates of Optimized Structures of $TS_{Nuc}$ (Ia → IVa)

E° = -2808.8898072; G° = -2808.229352; ν = -83.91; $E°_{(THF)}$ = -2808.9657528

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.494593379 | 2.6335745066 | 2.0308236636 | H | -3.4858087146 | 2.3193959572 | -1.1618105544 |
| C | -4.1156740981 | 1.7962601544 | 0.9372281861 | H | -3.8136767141 | 4.8828649798 | -0.3590161971 |
| C | -3.8016864923 | 2.6422673567 | -0.1698479362 | H | -4.6378873493 | 4.862905001 | 2.2097808105 |
| C | -3.9885564188 | 3.9948406404 | 0.2487885976 | H | -1.0017657804 | 5.3219969825 | 1.8657363538 |
| C | -4.4334801344 | 3.9844403961 | 1.5970043235 | H | -1.6010545627 | 3.6954575289 | 3.9587625141 |
| Fe | -2.5089712139 | 3.0192904901 | 1.4089004042 | H | -1.2485505771 | 1.1376489003 | 3.1416716752 |
| C | -0.9418403478 | 4.2335171174 | 1.8748504165 | H | -0.2806689417 | 3.7519378855 | -0.2185673534 |
| C | -1.257027273 | 3.3793178808 | 2.973725985 | C | 4.0546136728 | 1.1050971798 | 0.9337858521 |
| C | -1.0749964322 | 2.0296556237 | 2.5400274662 | C | 3.7292547146 | 0.2298740134 | 1.9210966504 |
| C | -0.4881600932 | 2.0456175781 | 1.2304897514 | N | 2.3917279066 | 0.4560611933 | 2.2171562635 |
| C | -0.5671965761 | 3.4033889909 | 0.7733374213 | C | 1.8662350281 | 1.4461924127 | 1.4501608476 |
| H | -4.7764943678 | 2.2954647493 | 3.0282181506 | N | 2.9036674644 | 1.8332200641 | 0.663688723 |
| H | -4.0840995731 | 0.7068962159 | 0.9480819207 | C | 2.8289309465 | 2.8743963463 | -0.3273509598 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.6600930938 | -0.2687299152 | 3.2230736837 | H | 3.3886936168 | 6.2073112007 | -0.6961456502 |
| C | 0.9462847073 | -1.4254530014 | 2.8434473438 | H | 3.5829458605 | 3.6482404131 | 2.0655372526 |
| C | 0.2447914438 | -2.1106040415 | 3.8441131286 | H | 5.5648652457 | 5.094131008 | 2.4162616065 |
| C | 0.2586396757 | -1.669193148 | 5.1651731407 | H | 5.7940107836 | 4.0773733651 | 0.9728662895 |
| C | 0.983327419 | -0.5325686648 | 5.5143638021 | H | 5.3783518353 | 5.7946750967 | 0.7926272364 |
| C | 1.7027483411 | 0.192967149 | 4.555527149 | H | 3.2273286532 | 5.8476458183 | 3.107533607 |
| C | 2.416884248 | 2.5391374254 | -1.6347305872 | H | 1.8088122171 | 5.3953653897 | 2.1315008485 |
| C | 2.3527759286 | 3.5725935302 | -2.5784666957 | H | 2.9638664081 | 6.6094759899 | 1.5283844611 |
| C | 2.6921319739 | 4.8803491395 | -2.2390602072 | H | 2.0351974921 | 0.503678351 | -1.1332484521 |
| C | 3.111022572 | 5.1798049291 | -0.9453989507 | H | 0.5257503582 | -0.0730511561 | -2.9755333019 |
| C | 3.1927424382 | 4.1866481041 | 0.0398003522 | H | -0.0687027387 | 1.4055561429 | -2.1785420152 |
| C | 3.6973255084 | 4.5403610421 | 1.4313083275 | H | 0.7613289124 | 1.503174821 | -3.7466407488 |
| C | 5.1913075523 | 4.8940852626 | 1.3993700798 | H | 3.0380598263 | -0.5252137634 | -3.1566942246 |
| C | 2.8759165177 | 5.6601989499 | 2.0805135644 | H | 4.2043862503 | 0.5636222695 | -2.3670119513 |
| C | 2.1023018577 | 1.1092545523 | -2.0502057263 | H | 3.3630458056 | 1.0843516859 | -3.842265385 |
| C | 0.7569563081 | 0.9850461157 | -2.7747354074 | H | 2.8854423331 | 1.8968193972 | 4.0637748902 |
| C | 3.2417751487 | 0.5265991121 | -2.899719026 | H | 4.3852464482 | 1.8379156467 | 6.034411269 |
| C | 2.5252648637 | 1.4013571571 | 4.9781613558 | H | 3.4716706523 | 0.4784652162 | 6.7273833503 |
| C | 3.7595812053 | 0.9668652619 | 5.7824128892 | H | 4.3825999401 | 0.2549893398 | 5.2191973542 |
| C | 1.6968951715 | 2.4342915206 | 5.7507362888 | H | 1.3338359276 | 2.0384966929 | 6.7126127426 |
| C | 0.9630080986 | -1.9652349213 | 1.4206337236 | H | 0.8225877406 | 2.7644025486 | 5.1689946984 |
| C | 1.8765985742 | -3.1956998733 | 1.3163616398 | H | 2.3074400155 | 3.3229208254 | 5.9763658836 |
| C | -0.4404609177 | -2.2767551307 | 0.887963789 | H | 1.3907784187 | -1.1837197037 | 0.7736975344 |
| H | 4.9907075039 | 1.2742549444 | 0.4075051434 | H | 2.9010338334 | -2.969845409 | 1.6497322707 |
| H | 4.3232230583 | -0.5219834274 | 2.4345999081 | H | 1.5011454947 | -4.0246487989 | 1.9376985044 |
| H | -0.3144783461 | -3.0136888119 | 3.5870481885 | H | 1.9310753176 | -3.5542742017 | 0.2760867131 |
| H | -0.2911569289 | -2.2228464102 | 5.9312546119 | H | -0.3918224232 | -2.5697014169 | -0.1727641583 |
| H | 0.998113619 | -0.2060289897 | 6.5573419014 | H | -1.1114248886 | -1.4067130266 | 0.9698522592 |
| H | 2.0424556061 | 3.3482819828 | -3.602258242 | H | -0.9132348296 | -3.1109460225 | 1.4300711699 |
| H | 2.6408687159 | 5.6706182705 | -2.993069652 | H | -0.4582961587 | 1.1842890215 | 0.5691744532 |

Coordinates of Optimized Structures of $TS_{Dep}$ (Ia → IIIa)

E° = -2808.8583355; G° = -2808.202763; ν = -1087.40; $E°_{(THF)}$ = -2808.9337068

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.3494141427 | 3.0543375242 | 1.426405802 | H | -1.8930607405 | 2.5984750641 | 3.8060752836 |
| C | -4.4325271126 | 1.6487003095 | 1.1905886767 | H | -1.6185137522 | 0.144132925 | 2.6733243183 |
| C | -3.9153172394 | 1.3794906023 | -0.1134673132 | H | -0.0905093084 | 3.1038260348 | -0.1481443333 |
| C | -3.5090523574 | 2.6202607947 | -0.6831776962 | C | 2.1302781882 | -1.8834137155 | -1.7875223321 |
| C | -3.7756276688 | 3.6561891904 | 0.2664974613 | C | 1.7619091846 | -2.7598828227 | -0.8136943791 |
| Fe | -2.4638575464 | 2.2773039131 | 1.0686604411 | N | 0.8546564168 | -2.0951713052 | -0.0058361564 |
| C | -0.9369569553 | 3.3437375054 | 1.917903233 | C | 0.6507655884 | -0.8385095392 | -0.454832512 |
| C | -1.4388240978 | 2.3761477399 | 2.8389788474 | N | 1.4373361333 | -0.7095432383 | -1.5443661603 |
| C | -1.2933760721 | 1.0851687386 | 2.2243195573 | C | 1.5513069776 | 0.4841247628 | -2.3467023203 |
| C | -0.7085707607 | 1.219618279 | 0.9176096641 | C | 0.2330781814 | -2.6768071197 | 1.1596319265 |
| C | -0.4919312554 | 2.6319769967 | 0.7513913463 | C | -0.9838807098 | -3.3707067095 | 0.999173783 |
| H | -4.6523527163 | 3.5733465494 | 2.3352666083 | C | -1.5507670786 | -3.944349692 | 2.1443597093 |
| H | -4.7929546394 | 0.9040030902 | 1.9005355186 | C | -0.9331546086 | -3.8326059801 | 3.3875990085 |
| H | -3.8241193577 | 0.3998129369 | -0.5788713606 | C | 0.2727712612 | -3.1477423076 | 3.5119416338 |
| H | -3.0417063238 | 2.7533774882 | -1.6582968994 | C | 0.8896097744 | -2.5563702588 | 2.4018814919 |
| H | -3.5600466104 | 4.716696454 | 0.1378873123 | C | 0.6802603842 | 0.6420327434 | -3.4435490498 |
| H | -0.9470548667 | 4.4247999898 | 2.066504564 | C | 0.8096109943 | 1.8121697309 | -4.202529958 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.7679632332 | 2.7723905696 | -3.8882092644 | H | 5.3319855442 | 1.8466732175 | -1.9651615893 |
| C | 2.6281216999 | 2.5773900438 | -2.8102761963 | H | 4.2084392063 | 2.1639067925 | 0.9638328334 |
| C | 2.5459239948 | 1.4274529898 | -2.0143835126 | H | 2.5184541227 | 2.5366018193 | 0.5481283603 |
| C | 3.5351067336 | 1.218411929 | -0.8769562431 | H | 3.8540576134 | 3.3214315845 | -0.3304934039 |
| C | 4.9491729547 | 0.9680304686 | -1.4217389541 | H | -0.2803131436 | -1.2362372714 | -3.1171720795 |
| C | 3.5230530492 | 2.3761756642 | 0.1281753514 | H | -2.5193008692 | -0.6345157721 | -3.9656080683 |
| C | -0.355442333 | -0.4027277174 | -3.8324858101 | H | -1.9901715192 | 0.5191097328 | -2.7127973185 |
| C | -1.7824758639 | 0.1494704955 | -3.7288449158 | H | -1.9494916887 | 0.9801332254 | -4.4332223014 |
| C | -0.0755032788 | -0.9777063127 | -5.2277315528 | H | -0.7944757158 | -1.7770836346 | -5.4672258646 |
| C | 2.2308838868 | -1.8562448099 | 2.5637534313 | H | 0.9379814229 | -1.4025509195 | -5.2952154597 |
| C | 3.3417043772 | -2.8655691748 | 2.8891842562 | H | -0.1647460426 | -0.2079590402 | -6.0106837281 |
| C | 2.1752788304 | -0.7323916297 | 3.6055845678 | H | 2.4868171483 | -1.3897031001 | 1.5998444352 |
| C | -1.6636235264 | -3.5409145455 | -0.3511943509 | H | 4.3186872513 | -2.3600874385 | 2.9478767703 |
| C | -1.5700340802 | -4.9942086967 | -0.8382662822 | H | 3.1651334799 | -3.3599367066 | 3.8578215376 |
| C | -3.1174349174 | -3.0541420199 | -0.3295775083 | H | 3.4145686511 | -3.6542884093 | 2.1241942923 |
| H | 2.8163363924 | -1.9883682921 | -2.624025726 | H | 1.9675708062 | -1.1202420643 | 4.6155118291 |
| H | 2.0610462793 | -3.7875142673 | -0.6242341678 | H | 1.3975958033 | 0.0070160151 | 3.3604805161 |
| H | -2.4908906809 | -4.4954460956 | 2.0601922818 | H | 3.1416255311 | -0.2059695523 | 3.6523441023 |
| H | -1.3923211708 | -4.2916159972 | 4.267374251 | H | -1.1252083515 | -2.9157690686 | -1.0803309347 |
| H | 0.7509440975 | -3.0777276011 | 4.4922584654 | H | -0.5253989754 | -5.3364938388 | -0.9001259943 |
| H | 0.1530118943 | 1.9702298085 | -5.0620764446 | H | -2.1028740176 | -5.6799225067 | -0.1602794689 |
| H | 1.8538771223 | 3.6766409982 | -4.4968879135 | H | -2.0193753256 | -5.0986995329 | -1.8386288005 |
| H | 3.386872782 | 3.3315310888 | -2.5862528068 | H | -3.554909115 | -3.1024875894 | -1.3394243152 |
| H | 3.232010423 | 0.3129111974 | -0.3287050965 | H | -3.1851263662 | -2.0141321927 | 0.0255559143 |
| H | 5.6490790978 | 0.7557701084 | -0.5980767074 | H | -3.7488637246 | -3.6733720988 | 0.3270086 |
| H | 4.9739346123 | 0.1136207364 | -2.1158216365 | H | -0.0792224984 | 0.1149787365 | 0.1248059041 |

Coordinates of Optimized Structures of cAAC

$E° = -834.6489144$; $G° = -834.234305$; $E°_{(THF)} = -834.6676093$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.0931656795 | -1.4881391372 | -2.417021243 | H | -2.0708841686 | -1.8919611546 | -2.1096955063 |
| C | 0.0402246165 | -2.4458570947 | -1.9559584083 | H | -1.1294962717 | -1.3658441384 | -3.5105628742 |
| C | 0.6483169293 | -1.8066690081 | -0.7179759481 | H | 1.5668933468 | -1.6081635351 | -3.3067239609 |
| N | 0.1410246533 | -0.6005426166 | -0.627790466 | H | 0.7725742743 | -3.0835367769 | -3.910325122 |
| C | -0.8446730649 | -0.1451173175 | -1.7065340198 | H | 1.9902666172 | -3.1839687751 | -2.6060557622 |
| C | 0.5182336655 | 0.2868092311 | 0.4490705818 | H | 0.3181714062 | -4.4870032359 | -1.240941534 |
| C | 1.1577107493 | -2.5849615731 | -3.0050739223 | H | -1.2605177783 | -3.7908786856 | -0.8159090341 |
| C | -0.4940597644 | -3.840337035 | -1.6061321007 | H | -0.9495843121 | -4.3168244479 | -2.4909981021 |
| C | -0.2046825787 | 0.9002314118 | -2.6265957046 | H | 0.0924311654 | 1.8006745603 | -2.0676700527 |
| C | -2.1185870464 | 0.4545105713 | -1.1113064498 | H | -0.9362343373 | 1.209687466 | -3.3895018933 |
| C | -0.2376657387 | 0.2715876189 | 1.6439576146 | H | 0.677438001 | 0.5085658667 | -3.1521190726 |
| C | 0.0883891269 | 1.1968650555 | 2.6436072404 | H | -2.7920203057 | 0.7557755311 | -1.9291955221 |
| C | 1.1464390055 | 2.0873113585 | 2.4866536027 | H | -1.9042161116 | 1.3505401555 | -0.50866873 |
| C | 1.9352026651 | 2.023993097 | 1.3424118021 | H | -2.662732094 | -0.2655693099 | -0.4850123165 |
| C | 1.6534696145 | 1.1172637376 | 0.3114801274 | H | -0.4878108236 | 1.2086319012 | 3.5720920217 |
| C | 2.6494641245 | 0.9528128567 | -0.827084204 | H | 1.3788028843 | 2.8090360022 | 3.2749206323 |
| C | 3.1584894835 | 2.2770277838 | -1.4031981242 | H | 2.8038771495 | 2.681250561 | 1.2541193142 |
| C | 3.8095382654 | 0.0594797877 | -0.3596430451 | H | 2.147006071 | 0.4099547132 | -1.6369478391 |
| C | -1.2798267871 | -0.8005397162 | 1.9293904821 | H | 3.7871852953 | 2.0908236807 | -2.288876349 |
| C | -0.6298049798 | -1.9389443452 | 2.731590341 | H | 3.7801758537 | 2.8316768221 | -0.681988389 |
| C | -2.5396519642 | -0.2727175188 | 2.6208215833 | H | 2.3324715856 | 2.9387285213 | -1.7086940571 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 3.4304491646 | -0.9179339274 | -0.0243447797 | H | 0.2261235553 | -2.3581295043 | 2.1807610635 |
| H | 4.3557961349 | 0.5252931706 | 0.477126768 | H | -0.2685796679 | -1.5784918186 | 3.708862466 |
| H | 4.5262612684 | -0.1096484182 | -1.1805990463 | H | -3.292990139 | -1.0727013086 | 2.7034356188 |
| H | -1.5867514606 | -1.2353106509 | 0.9686063853 | H | -2.9929118075 | 0.5637927239 | 2.0657094213 |
| H | -1.354988979 | -2.7491806956 | 2.9154381185 | H | -2.3346278123 | 0.0786325597 | 3.6449673941 |

Coordinates of Optimized Structures of $cAACH^{+}$

$E° = -835.0715535$; $G° = -834.641171$; $E°_{(THF)} = -835.1451421$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.689825682 | 0.0160508443 | -2.0477866389 | H | -2.5824143255 | -2.699781847 | -1.550213996 |
| C | -2.015923338 | -0.770072601 | -0.7518362715 | H | -0.8286952825 | -2.5567216037 | -1.30268209 |
| C | -1.0093349291 | -0.191843245 | 0.18736734 | H | -1.911047675 | -2.8000459198 | 0.0918833634 |
| N | -0.1248235407 | 0.5672375554 | -0.3530774232 | H | -0.2384714946 | 1.9662206879 | -3.5339584347 |
| C | -0.2698952849 | 0.6034951644 | -1.8891624326 | H | 0.8860415504 | 2.4180872771 | -2.2367444769 |
| C | 0.892141662 | 1.3337305224 | 0.3565376529 | H | -0.8655764328 | 2.7074023503 | -2.0504897207 |
| C | -3.4397249346 | -0.5047402376 | -0.2298806862 | H | 1.8051195647 | 0.1294303376 | -2.3471534732 |
| C | -1.808618667 | -2.2948182615 | -0.8806478268 | H | 0.7715944592 | -1.318702894 | -2.1650160619 |
| C | -0.1158506045 | 2.0137668187 | -2.4415843059 | H | 0.6364244899 | -0.2948285577 | -3.6080955544 |
| C | 0.8021699574 | -0.2808134441 | -2.5209020639 | H | 4.2180260945 | 1.3927265193 | 1.031430413 |
| C | 2.2088716285 | 0.8275243251 | 0.505640573 | H | 3.6914554022 | 3.7668767483 | 1.4821773028 |
| C | 3.1916410161 | 1.7502947681 | 0.9083647814 | H | 1.3201636798 | 4.4898805343 | 1.5495207936 |
| C | 2.8978564584 | 3.0732853587 | 1.193547943 | H | -0.6829736852 | 4.1655989963 | 1.5441957553 |
| C | 1.5679747567 | 3.4827098697 | 1.2038252295 | H | -2.8359742356 | 3.7955122445 | 0.5443360923 |
| C | 0.5239197082 | 2.6319346281 | 0.8217228862 | H | -1.6033078571 | 4.0039514991 | -0.7050193528 |
| C | -0.88259232 | 3.146639151 | 1.1784702166 | H | -2.2785320603 | 2.3866949264 | -0.3607294664 |
| C | -1.9452744101 | 3.3304062542 | 0.0939353579 | H | -2.293649453 | 2.9534010195 | 2.8234833682 |
| C | -1.4505230554 | 2.3911109728 | 2.3925386447 | H | -0.694986352 | 2.2632043372 | 3.1823211461 |
| C | 2.7199773811 | -0.6274713101 | 0.4775809658 | H | -1.8418717687 | 1.395139488 | 2.1312935356 |
| C | 1.7086894992 | -1.7543278559 | 0.6854946501 | H | 3.3328583574 | -0.6453376096 | 1.3953298681 |
| C | 3.7068886223 | -0.9484333591 | -0.6562899776 | H | 2.2528830787 | -2.6899163848 | 0.885690564 |
| H | -1.757488417 | -0.6193198677 | -2.9415496807 | H | 1.0639062075 | -1.571563487 | 1.559316201 |
| H | -2.4161361037 | 0.8322818071 | -2.178143092 | H | 1.077303325 | -1.9478363645 | -0.1919814659 |
| H | -0.9916348386 | -0.3688107067 | 1.2670038518 | H | 3.2092270986 | -1.1270517334 | -1.6189208603 |
| H | -3.6320990517 | -1.0458892186 | 0.7094231491 | H | 4.2677621769 | -1.8630401407 | -0.4093259775 |
| H | -4.1678510898 | -0.8602634345 | -0.974906175 | H | 4.4405655106 | -0.1416762272 | -0.8016321966 |
| H | -3.628913796 | 0.5652523054 | -0.059064944 | | | | |

Coordinates of Optimized Structures of $cAAC^{+}$

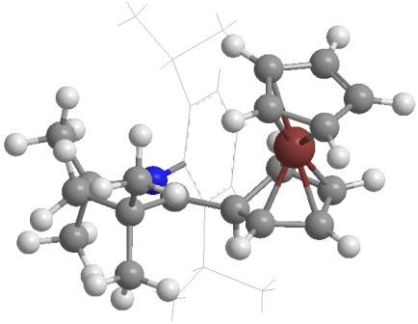
$E° = -834.3851648$; $G° = -833.969591$; $E°_{(THF)} = -834.4566036$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.6855514801 | 0.0125243102 | -2.0260448622 | C | 2.2651162719 | 0.8446713265 | 0.4887038674 |
| C | -2.0413386793 | -0.7438745211 | -0.6999091358 | C | 3.2314267473 | 1.7848673892 | 0.8911106723 |
| C | -0.996539588 | -0.1344094183 | 0.1676735782 | C | 2.9073749007 | 3.0956041388 | 1.2044073554 |
| N | -0.0729339567 | 0.5577202273 | -0.3542062657 | C | 1.5671235509 | 3.4726251063 | 1.2452562027 |
| C | -0.2432957482 | 0.5699399492 | -1.9131495266 | C | 0.54448449 | 2.6012882714 | 0.8571813909 |
| C | 0.9419815703 | 1.3288182928 | 0.3573323669 | C | -0.8824992566 | 3.0330415203 | 1.2277590835 |
| C | -3.4613783436 | -0.4339462486 | -0.204424773 | C | -1.8837910207 | 3.356931384 | 0.1159086019 |
| C | -1.8459261422 | -2.2701187633 | -0.7833075876 | C | -1.4791237299 | 2.0930285857 | 2.284667421 |
| C | -0.0751952695 | 1.9783048852 | -2.4584906456 | C | 2.7754633449 | -0.607255525 | 0.4612733687 |
| C | 0.791697852 | -0.3442988147 | -2.5523441551 | C | 1.7467572692 | -1.7239614318 | 0.6377636089 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.7807333974 | -0.9209001809 | -0.6571063324 | H | 3.6878112364 | 3.8017752675 | 1.498506443 |
| H | -1.7864113102 | -0.6539965457 | -2.8942659861 | H | 1.2963466202 | 4.4626684797 | 1.6224734996 |
| H | -2.3942019469 | 0.8421554175 | -2.1637534767 | H | -0.724658424 | 3.9914898122 | 1.7472514179 |
| H | -3.6676010854 | -0.9398702648 | 0.7501741759 | H | -2.7857216401 | 3.8039108237 | 0.5622552705 |
| H | -4.1848758918 | -0.8030369952 | -0.9471527971 | H | -1.4783454614 | 4.0912588234 | -0.5959888386 |
| H | -3.6309009966 | 0.6440212043 | -0.0712250258 | H | -2.2164231946 | 2.4729040301 | -0.447364183 |
| H | -2.5985077985 | -2.6799944135 | -1.4736099266 | H | -2.4249608037 | 2.4997750953 | 2.6761052943 |
| H | -0.8526414769 | -2.5530811924 | -1.1566758954 | H | -0.7910223157 | 1.9483223449 | 3.1309881625 |
| H | -1.9934878493 | -2.7422006614 | 0.1988340341 | H | -1.7083031925 | 1.0873057641 | 1.87982943 |
| H | -0.2482052015 | 1.9442441806 | -3.5454233035 | H | 3.368808343 | -0.6335345281 | 1.3920012932 |
| H | 0.946551391 | 2.3508222612 | -2.294988642 | H | 2.2697216118 | -2.6563339279 | 0.8999988956 |
| H | -0.7859187767 | 2.6895959318 | -2.0267744617 | H | 1.040886712 | -1.5102522724 | 1.456731558 |
| H | 1.8092704523 | 0.0295541261 | -2.3821701396 | H | 1.1751073031 | -1.9366608328 | -0.2751781343 |
| H | 0.7267052437 | -1.3841059919 | -2.2072769774 | H | 3.3015981872 | -1.0474972141 | -1.6378721013 |
| H | 0.6183102439 | -0.3432664847 | -3.6391908734 | H | 4.305986905 | -1.8616064029 | -0.4308779726 |
| H | 4.2670702245 | 1.4499264972 | 0.9996429297 | H | 4.542972712 | -0.133806815 | -0.7558789025 |

Coordinates of Optimized Structures of **[**FcH-cAAC]$^{+}$ Isomer 1 (IVb-1)

E° = -2484.7207756; G° = -2484.142098; E°$_{(THF)}$ = -2484.7930802

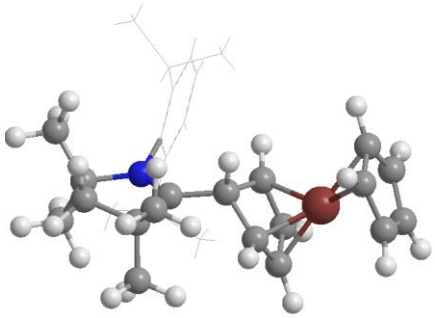


| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.1271189523 | -5.4445888052 | -0.0236700588 | C | 2.0193583816 | 2.9501429826 | 0.5175405851 |
| C | 0.2244731348 | -4.1487986959 | 1.6570247073 | C | 2.1633754126 | 2.8567591558 | 1.8954169959 |
| C | 1.6326759181 | -4.240835198 | 1.8632009419 | C | 1.3286963736 | 2.010329192 | 2.6154412123 |
| C | 2.1816323956 | -5.064220451 | 0.84602677 | C | 0.3237749572 | 1.2606498052 | 1.9920928484 |
| C | 0.6012836324 | -2.4538647323 | -1.7547069396 | C | 1.0247281878 | 2.3667016985 | -1.6954005726 |
| C | 0.5030443974 | -1.0744672461 | -1.0966587294 | C | -0.490070956 | 0.3164370961 | 2.8736875093 |
| C | 1.6075603036 | -1.3286491244 | -0.0568965674 | C | 0.8181136697 | 3.8174306176 | -2.1571097565 |
| C | 2.6172686909 | -2.1017961362 | -0.7095884011 | C | 2.3236090829 | 1.81779008 | -2.312344791 |
| C | 1.9899964828 | -2.802310258 | -1.7775388928 | C | 0.3752105608 | -0.8405153073 | 3.395856585 |
| Fe | 1.1816058825 | -3.3228862166 | -0.0277865087 | C | -1.1466148884 | 1.0388107383 | 4.0605061426 |
| C | -0.0923531341 | -4.8894848266 | 0.4818698045 | H | 1.2232779111 | -6.0706717809 | -0.9108755653 |
| C | -0.8067848553 | -0.4476966802 | -0.7349027068 | H | -0.4787918204 | -3.6209986417 | 2.3000266487 |
| N | -0.9104184838 | 0.6777329811 | -0.0689536957 | H | 2.1926063533 | -3.7679747907 | 2.6702407799 |
| C | 0.1771707209 | 1.3959187799 | 0.5861978966 | H | 3.2350619238 | -5.3178039921 | 0.7276825856 |
| C | -2.3086860085 | 1.3035216427 | -0.1624648948 | H | -0.094442622 | -2.8277922895 | -2.5056745008 |
| C | -2.8104711447 | 1.8550399562 | 1.1649427272 | H | 0.8472274726 | -0.3037080978 | -1.8333521883 |
| C | -3.1278846828 | 0.1004767117 | -0.6377950106 | H | 1.8258354486 | -0.647876299 | 0.7634933517 |
| C | -2.2880797219 | 2.4477652289 | -1.1783175573 | H | 3.6596739816 | -2.1912522755 | -0.4009620651 |
| C | -2.1483080907 | -0.8908473823 | -1.2981267962 | H | 2.4608680909 | -3.526242423 | -2.4437979275 |
| C | -2.5087480207 | -2.3285532383 | -0.8896320203 | H | -1.0851237329 | -5.0562710038 | 0.0660412353 |
| C | -2.1464841224 | -0.7637628919 | -2.8370400195 | H | -3.8014125484 | 2.3005718767 | 0.9912804541 |
| C | 1.0377679724 | 2.2283337161 | -0.1753478474 | H | -2.1561275571 | 2.6481654278 | 1.553826245 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -2.931034296 | 1.076763641 | 1.9276082431 | H | 0.1888403893 | 1.7698897479 | -2.0920450751 |
| H | -3.9315370052 | 0.4049260146 | -1.3225195686 | H | -1.2868291481 | -0.129729742 | 2.2595475548 |
| H | -3.6069633813 | -0.3791438337 | 0.229304165 | H | 0.7182099129 | 3.8574203679 | -3.2530857186 |
| H | -3.3104921483 | 2.8411150887 | -1.277010173 | H | 1.6791070545 | 4.4487472495 | -1.8882694123 |
| H | -1.9537909423 | 2.1344720594 | -2.1759472215 | H | -0.0769022528 | 4.2814927451 | -1.7191709804 |
| H | -1.6499106909 | 3.2721981543 | -0.8341136715 | H | 2.2562961128 | 1.8201411997 | -3.4116149728 |
| H | -3.543799312 | -2.5293001852 | -1.2077170816 | H | 2.550067691 | 0.7919042967 | -1.984199052 |
| H | -2.4632807563 | -2.460516835 | 0.2019815495 | H | 3.1873298456 | 2.4421988754 | -2.0360497242 |
| H | -1.8572787885 | -3.0792037156 | -1.3513638373 | H | -0.2287094561 | -1.5061586426 | 4.0332067941 |
| H | -3.1428818131 | -1.0390328692 | -3.2150183569 | H | 1.2092265078 | -0.4677471439 | 4.0111799538 |
| H | -1.4152603969 | -1.4330761409 | -3.3091992099 | H | 0.7961592264 | -1.4393698906 | 2.576791894 |
| H | -1.9335701405 | 0.26106525 | -3.1729743961 | H | -1.7115947481 | 1.931776195 | 3.7588764364 |
| H | 2.6932582342 | 3.5999998828 | -0.0454239574 | H | -0.3946579172 | 1.3597106359 | 4.7979052681 |
| H | 2.9352907917 | 3.4360898895 | 2.4084883991 | H | -1.8365803844 | 0.358535536 | 4.5840349667 |
| H | 1.46143591 | 1.9232102661 | 3.6961751717 | | | | |

Coordinates of Optimized Structures of [FcH-cAAC]$^{+}$ Isomer 2 (IVb-2)
: More stable than IVb-1 (-4.8 kcal/mol)

E° = -2484.7282254; G° = -2484.149823; E°$_{(THF)}$ = -2484.8005803

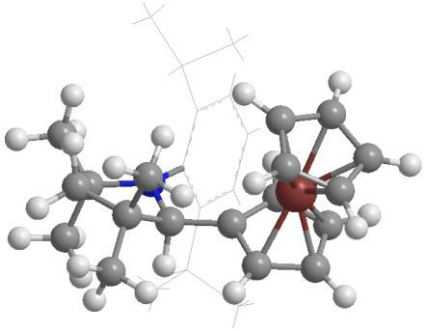


| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.6566418491 | -2.4479444377 | -0.8818310204 | C | 2.0377662292 | 5.5687222639 | -1.166364927 |
| C | 0.7223581007 | -0.9750270183 | 0.8907917006 | C | 1.8775149155 | 5.6532076643 | 0.2107879114 |
| C | 2.0376010788 | -1.0829544212 | 0.3380141694 | C | 0.6906026531 | 5.2203179913 | 0.790484081 |
| C | 1.9987812216 | -2.0158871855 | -0.7289952063 | C | -0.3564311055 | 4.6970021642 | 0.0221358088 |
| C | -0.7131396357 | 0.335380164 | -2.4226355797 | C | 1.3251562277 | 5.0073623948 | -3.4938140044 |
| C | -0.8219410778 | 1.6512726024 | -1.6384062457 | C | -1.6034955291 | 4.232452612 | 0.7721040728 |
| C | 0.6495693719 | 1.6996704409 | -1.2286618675 | C | 1.5630486416 | 6.4161625053 | -4.0622735443 |
| C | 1.4469979212 | 1.0858782509 | -2.2465993283 | C | 2.5225379758 | 4.1092030098 | -3.8315898408 |
| C | 0.5908932986 | 0.2361754533 | -3.0047252461 | C | -1.302938454 | 3.0455873969 | 1.7029880004 |
| Fe | 0.6374173779 | -0.3216238273 | -1.0853675695 | C | -2.2422876906 | 5.3676113684 | 1.5887956885 |
| C | -0.13670443 | -1.8231189184 | 0.1313569494 | H | 0.2932453934 | -3.1491118068 | -1.6334420543 |
| C | -1.552602911 | 2.8156292999 | -2.2918077045 | H | 0.4443562761 | -0.3750908825 | 1.757083542 |
| N | -1.2570979431 | 4.0824598555 | -2.1879623602 | H | 2.9215580613 | -0.5496741957 | 0.68817298 |
| C | -0.1653690604 | 4.6212419454 | -1.3832852973 | H | 2.8404824203 | -2.3055456596 | -1.3582893867 |
| C | -2.3073812356 | 5.002335218 | -2.8424871101 | H | -1.5710527409 | -0.2403640112 | -2.7684357502 |
| C | -2.6555640811 | 6.1687810237 | -1.9271760054 | H | -1.4692114169 | 1.4873030228 | -0.7515305161 |
| C | -3.4704156053 | 4.0171882004 | -3.009679509 | H | 1.0512208936 | 2.3834174125 | -0.4824830039 |
| C | -1.8343573871 | 5.5548033583 | -4.1885527994 | H | 2.5274168233 | 1.1775232065 | -2.3604907347 |
| C | -2.866078496 | 2.59876909 | -3.0293890389 | H | 0.8890341613 | -0.4277134261 | -3.8173366667 |
| C | -3.7994143536 | 1.6186842816 | -2.2992477458 | H | -1.1992905152 | -1.9944409646 | 0.3028220588 |
| C | -2.6026333327 | 2.0934437726 | -4.4649527217 | H | -3.4311476107 | 6.7729490578 | -2.4214123489 |
| C | 1.0330235444 | 5.0569491067 | -1.9986408473 | H | -1.7897201715 | 6.8213349687 | -1.7435484092 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -3.061219729 | 5.8347605171 | -0.9647581585 | H | 0.4532849558 | 4.5711823314 | -3.9990812507 |
| H | -4.0567512551 | 4.2292506359 | -3.914350343 | H | -2.3513615013 | 3.894876086 | 0.0363579452 |
| H | -4.1550199511 | 4.10892884 | -2.1518188494 | H | 1.6081129128 | 6.3854126149 | -5.1622094949 |
| H | -2.6797777024 | 6.0916741962 | -4.6438722991 | H | 2.5214440441 | 6.828396965 | -3.7096374849 |
| H | -1.5230724031 | 4.7716141441 | -4.8922249829 | H | 0.7813292177 | 7.1343366144 | -3.7710733991 |
| H | -1.0165994486 | 6.2744700186 | -4.0741475397 | H | 2.6867028695 | 4.0954857531 | -4.9206065355 |
| H | -4.7820449569 | 1.6360204524 | -2.7956768147 | H | 2.359692088 | 3.0757540454 | -3.5014982235 |
| H | -3.9560668334 | 1.9073232558 | -1.2482055748 | H | 3.4511705146 | 4.4740289951 | -3.365422627 |
| H | -3.4373476411 | 0.5830155076 | -2.3247515269 | H | -2.2320802769 | 2.6814789204 | 2.1693020549 |
| H | -3.5623296505 | 2.0384968411 | -5.0012412371 | H | -0.6253917841 | 3.3443562854 | 2.5181383589 |
| H | -2.1529678891 | 1.0925219269 | -4.4686787827 | H | -0.8293407863 | 2.2027147227 | 1.1792984891 |
| H | -1.9379586007 | 2.7603003929 | -5.0309502151 | H | -2.4321610287 | 6.2678458567 | 0.9870503 |
| H | 2.9748242646 | 5.9060792346 | -1.6154190768 | H | -1.5965202116 | 5.6683602002 | 2.4282346505 |
| H | 2.6789096169 | 6.0575803446 | 0.8345042878 | H | -3.1994402229 | 5.0352644116 | 2.0203390387 |
| H | 0.5705787361 | 5.2875385422 | 1.8742757184 | | | | |

Coordinates of Optimized Structures of [Fc-cAAC-H]$^+$ Isomer 1 (Vb-1)

E° = -2484.7092458; G° = -2484.130234; E°$_{(THF)}$ = -2484.7861524



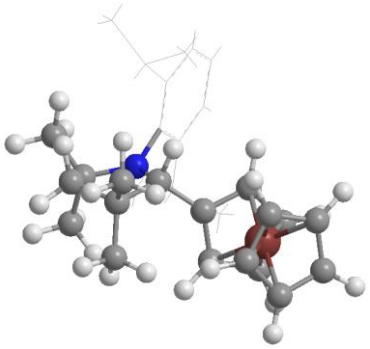
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.0318999241 | -2.1049556416 | -0.8834807828 | C | 1.9381837069 | 5.8493757623 | 0.1089842927 |
| C | -1.2572059983 | -0.6238759013 | 0.3316757048 | C | 0.8366041575 | 5.3891700868 | 0.8230219427 |
| C | 0.0643708588 | -0.6038265127 | 0.8710484137 | C | -0.2563315856 | 4.7958656446 | 0.1794308873 |
| C | 0.8631128085 | -1.5208107839 | 0.1222897056 | C | 1.0032270852 | 5.106816086 | -3.4951642614 |
| C | 0.12387135 | 0.6557650407 | -3.08738898 | C | -1.3838133372 | 4.2627055158 | 1.0569691819 |
| C | -0.202813556 | 1.7923053067 | -2.2717690898 | C | 1.1996893555 | 6.5052719696 | -4.0999002283 |
| C | 0.8536269485 | 1.8949236636 | -1.3048435509 | C | 2.1343446755 | 4.1733741294 | -3.9510899381 |
| C | 1.8539333239 | 0.9130722691 | -1.5899392899 | C | -0.9293981561 | 3.0576400219 | 1.8921870668 |
| C | 1.3995692005 | 0.1414266188 | -2.7031858151 | C | -1.9757041198 | 5.339748771 | 1.9759403705 |
| Fe | 0.1272892691 | -0.0501018957 | -1.1261331624 | H | 0.3463328806 | -2.8326302953 | -1.6317411099 |
| C | -1.2770243561 | -1.5515411134 | -0.7496722896 | H | -2.0954850927 | -0.0190194125 | 0.6736367454 |
| C | -1.2609101363 | 2.8110140877 | -2.6580062216 | H | 0.4104443422 | 0.0219885706 | 1.6935105903 |
| N | -1.3702924954 | 4.0164990782 | -1.8566238973 | H | 1.921481199 | -1.7275406967 | 0.2795909272 |
| C | -0.2495073619 | 4.674246916 | -1.2434097161 | H | -0.4843340936 | 0.2701890977 | -3.9050726031 |
| C | -2.5493152279 | 4.7774351579 | -2.368278774 | H | 0.9030153616 | 2.6219866073 | -0.4970173456 |
| C | -3.0571890017 | 5.8214006094 | -1.3772754896 | H | 2.7875263051 | 0.7777192012 | -1.0445378144 |
| C | -3.5558500691 | 3.6332193793 | -2.5584369246 | H | 1.9177057323 | -0.6990284775 | -3.1649467473 |
| C | -2.2987398435 | 5.4976114912 | -3.7070238168 | H | -2.1354245408 | -1.78864327 | -1.3771994852 |
| C | -2.7554384514 | 2.3419751687 | -2.8723049206 | H | -0.8939724067 | 3.0503081217 | -3.6841250288 |
| C | -3.1831100278 | 1.2471894063 | -1.8989678726 | H | -3.9214164142 | 6.3444451803 | -1.8136494598 |
| C | -2.9954730356 | 1.8712026952 | -4.3120421701 | H | -2.2886103402 | 6.5786766545 | -1.1600348452 |
| C | 0.8713967345 | 5.1597397886 | -1.9755182948 | H | -3.3866969399 | 5.3724234557 | -0.4318172175 |
| C | 1.9467849585 | 5.7268061602 | -1.2742865476 | H | -4.2866820053 | 3.8607572764 | -3.3483028648 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -4.1241002166 | 3.498626822 | -1.6258291556 | H | -2.1709675242 | 3.9064175766 | 0.3788831045 |
| H | -3.2379336601 | 5.9495987467 | -4.0610484451 | H | 1.1629666967 | 6.4573944464 | -5.1999124429 |
| H | -1.9499277722 | 4.823633724 | -4.5041459155 | H | 2.1759661216 | 6.9337428854 | -3.8245890295 |
| H | -1.5678863518 | 6.3097382207 | -3.5938191825 | H | 0.4263560609 | 7.21295245 | -3.7649251852 |
| H | -4.2702322491 | 1.0839323213 | -1.9703433268 | H | 2.1847226883 | 4.1360630891 | -5.0511901708 |
| H | -2.9556536383 | 1.5359190171 | -0.8615170411 | H | 1.9950020271 | 3.144431943 | -3.5864308337 |
| H | -2.6927848382 | 0.2883455354 | -2.1187903561 | H | 3.1152866324 | 4.5215112333 | -3.5900041485 |
| H | -4.0601828992 | 1.6340652143 | -4.4637042337 | H | -1.7626841976 | 2.6725763868 | 2.50286894 |
| H | -2.4290721616 | 0.9579506181 | -4.5572776201 | H | -0.1123247961 | 3.3245048383 | 2.5821549584 |
| H | -2.7213156696 | 2.6427241621 | -5.0478965677 | H | -0.5730247584 | 2.2366668507 | 1.2513726784 |
| H | 2.8109859823 | 6.0945680495 | -1.8338845296 | H | -2.271963446 | 6.2409117333 | 1.4201256131 |
| H | 2.7841749741 | 6.306612072 | 0.6292913486 | H | -1.2577031886 | 5.6529599721 | 2.7506497391 |
| H | 0.8291418818 | 5.4870926651 | 1.9121396867 | H | -2.8667029847 | 4.9548102422 | 2.4976124156 |
| H | 0.0670937023 | 4.7119051945 | -3.9043505732 | | | | |

Coordinates of Optimized Structures of [Fc-cAAC-H]$^{+}$ Isomer 2 (Vb-2)

: More stable than Vb-1 (-20.7 kcal/mol)

E° = -2484.7432835; G° = -2484.163212; E°$_{(THF)}$ = -2484.7943507



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.0805304385 | -2.2824650235 | -2.1876337734 | C | 1.9326738277 | 5.852225119 | -1.1257870718 |
| C | -0.7013040263 | -1.2722137842 | -0.2076134289 | C | 1.7379752798 | 6.0927400845 | 0.2286105325 |
| C | 0.6722472684 | -1.6456287063 | -0.1075607593 | C | 0.5551801629 | 5.6758124607 | 0.8300584359 |
| C | 1.0493588117 | -2.2726756779 | -1.3261361509 | C | -0.4470095947 | 5.0193632468 | 0.1046411615 |
| C | 0.1400482658 | 1.1143828992 | -3.2442924261 | C | 1.2743914236 | 4.9577328912 | -3.3703350834 |
| C | -0.2339521896 | 1.7866818098 | -2.0369262951 | C | -1.7340783226 | 4.6776028913 | 0.8492798424 |
| C | 0.8936595774 | 1.6905289622 | -1.1604258261 | C | 1.2054205845 | 6.2809043442 | -4.1481039068 |
| C | 1.955748044 | 1.0122190313 | -1.8252579018 | C | 2.6286621113 | 4.2799491013 | -3.6142633389 |
| C | 1.4858785018 | 0.6546174592 | -3.1243210995 | C | -1.5140625128 | 3.6190770101 | 1.9410789486 |
| Fe | 0.3685542691 | -0.2765555844 | -1.6779221504 | C | -2.3913475391 | 5.9240545853 | 1.4626870186 |
| C | -1.1677968317 | -1.6694933946 | -1.4993276358 | H | -0.1041576951 | -2.6734630409 | -3.2053354016 |
| C | -1.4532765402 | 2.6091014664 | -1.6448375183 | H | -1.2885575883 | -0.7812241049 | 0.5684105894 |
| N | -1.1895031723 | 3.9917619738 | -2.0358462907 | H | 1.3265756907 | -1.4635910273 | 0.7455055213 |
| C | -0.2305875374 | 4.7406152228 | -1.2780950019 | H | 2.0463701426 | -2.6377553497 | -1.5754140591 |
| C | -2.3147546329 | 4.5859603046 | -2.8138903127 | H | -0.4843614111 | 0.9695760307 | -4.1219023823 |
| C | -2.602737371 | 6.0279791815 | -2.3941472756 | H | 0.9244986303 | 2.0869607757 | -0.1451937671 |
| C | -3.4781557876 | 3.6539401527 | -2.4278689399 | H | 2.9441294359 | 0.8057251648 | -1.4141978813 |
| C | -2.0582096703 | 4.5789425202 | -4.3332635762 | H | 2.0478412195 | 0.1198531662 | -3.8906247994 |
| C | -2.8897947189 | 2.2498072301 | -2.1638519904 | H | -2.1773472334 | -1.5398268144 | -1.8878251686 |
| C | -3.6776371117 | 1.5300482126 | -1.0595844438 | H | -1.485641649 | 2.533685627 | -0.544496222 |
| C | -2.9713091676 | 1.381900573 | -3.4276769359 | H | -3.4562443049 | 6.4143831007 | -2.9720312988 |
| C | 0.9768049077 | 5.1738548818 | -1.8944363568 | H | -1.742324108 | 6.6845614675 | -2.5899196834 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -2.8541331491 | 6.10419343 | -1.3283916609 | H | 0.4922179067 | 4.2890995847 | -3.7572210503 |
| H | -4.2702234761 | 3.6301455015 | -3.1918962806 | H | -2.4458473037 | 4.2706023021 | 0.1164475301 |
| H | -3.9408660207 | 4.033780218 | -1.503093251 | H | 1.3247005786 | 6.1079056709 | -5.2299860531 |
| H | -2.9813795636 | 4.832452524 | -4.8776882867 | H | 2.0078397244 | 6.9670523166 | -3.8322806387 |
| H | -1.709483394 | 3.6023163908 | -4.6961147201 | H | 0.2516150818 | 6.8067712298 | -3.9912927467 |
| H | -1.3005451937 | 5.3233817072 | -4.6110132457 | H | 2.7552139122 | 4.0499885375 | -4.6845596122 |
| H | -4.7219374486 | 1.3670984445 | -1.3692177097 | H | 2.7231903165 | 3.3398823962 | -3.0507183074 |
| H | -3.6945636677 | 2.1112052937 | -0.124540278 | H | 3.472276427 | 4.9256861473 | -3.3231371348 |
| H | -3.2466869941 | 0.5411099232 | -0.8326245136 | H | -2.466287374 | 3.3564637081 | 2.4295150997 |
| H | -4.0290214779 | 1.2532853496 | -3.7045298367 | H | -0.8349748649 | 3.9911517304 | 2.72460895 |
| H | -2.561255837 | 0.3738826752 | -3.264465859 | H | -1.0741365789 | 2.6891465524 | 1.5445913335 |
| H | -2.4705176763 | 1.8254902153 | -4.2978421852 | H | -2.5373907227 | 6.7219070571 | 0.7193061123 |
| H | 2.8558369494 | 6.1948408435 | -1.6007830429 | H | -1.7829025242 | 6.3440741741 | 2.2785559773 |
| H | 2.4997816733 | 6.6157862028 | 0.8130636953 | H | -3.3759687403 | 5.6703778493 | 1.8871665119 |
| H | 0.395437438 | 5.8885125839 | 1.890672307 | | | | |

Coordinates of Optimized Structures of [Fc-cAAC] radical (VIb)

E° = -2484.3412915; G° = -2483.775254; $E°_{(THF)}$ = -2484.3627621

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.1915895985 | -2.0435843632 | -0.7270224296 | H | -0.0493703467 | -2.8552693675 | -1.4406747093 |
| C | -1.1325483655 | -0.2850860703 | 0.4373509083 | H | -1.8310178928 | 0.4798265644 | 0.7751259689 |
| C | 0.1877610687 | -0.4972552553 | 0.9388386776 | H | 0.6725691322 | 0.0725772564 | 1.7311298991 |
| C | 0.7628891926 | -1.5928511022 | 0.2289968125 | H | 1.7666323882 | -1.9925781191 | 0.3728817222 |
| C | 0.1636534394 | 0.5155614036 | -3.0412319551 | H | -0.4941022666 | 0.1093792533 | -3.8058104236 |
| C | -0.0542347721 | 1.7448557541 | -2.2922661817 | H | 1.2326991364 | 2.5807271485 | -0.6252115481 |
| C | 1.0700986271 | 1.8102289004 | -1.3724242639 | H | 2.9674226589 | 0.6258730395 | -1.1977662863 |
| C | 2.0053456497 | 0.7811278605 | -1.6858676597 | H | 1.8969974817 | -0.8995289288 | -3.1779687531 |
| C | 1.4454422483 | -0.0176454999 | -2.7235310262 | H | -2.275630651 | -1.3414506278 | -1.1833759622 |
| Fe | 0.2636950937 | -0.0580594824 | -1.0780039213 | H | -4.0542471555 | 5.8768021253 | -1.5484117106 |
| C | -1.3642733095 | -1.2377132138 | -0.596566768 | H | -2.4932956949 | 6.1953385765 | -0.7661525129 |
| C | -1.1385825547 | 2.6485154766 | -2.4593985831 | H | -3.418006586 | 4.7195557897 | -0.3611983905 |
| N | -1.211631822 | 3.9345330927 | -1.9099028301 | H | -4.0078499754 | 3.8369673377 | -3.6330435196 |
| C | -0.0949844894 | 4.6512112647 | -1.3630981834 | H | -3.954033514 | 3.1594319154 | -1.9979608801 |
| C | -2.4476398874 | 4.6652524625 | -2.3282484088 | H | -3.1159502608 | 6.2064481872 | -3.7002287291 |
| C | -3.1341493777 | 5.4003626849 | -1.174864649 | H | -1.7482153251 | 5.2699629249 | -4.3332161861 |
| C | -3.3265004847 | 3.5130834553 | -2.8313838083 | H | -1.4840006568 | 6.4844727671 | -3.0571530763 |
| C | -2.1735104315 | 5.7091949373 | -3.4224240745 | H | -4.0683888659 | 0.9883924314 | -3.4314863143 |
| C | -2.3969543908 | 2.3657646562 | -3.2777574967 | H | -3.2292628456 | 0.9246857423 | -1.8588788588 |
| C | -3.0798914741 | 1.029734622 | -2.943836062 | H | -2.505240177 | 0.1594544734 | -3.2875889619 |
| C | -2.1272148933 | 2.4177059347 | -4.7967914454 | H | -3.0668508386 | 2.275125293 | -5.3571333383 |
| C | 0.9497227029 | 5.1279738399 | -2.2046375673 | H | -1.4280394315 | 1.6279875815 | -5.1082967117 |
| C | 1.9879539034 | 5.8732235402 | -1.6306283361 | H | -1.6946170731 | 3.3784573503 | -5.1098980418 |
| C | 2.0237238011 | 6.1506410163 | -0.2688975271 | H | 2.7913376462 | 6.2461590952 | -2.2717215745 |
| C | 1.022689388 | 5.64761428 | 0.553540099 | H | 2.84009382 | 6.7439083398 | 0.1528660923 |
| C | -0.0338567162 | 4.8841870471 | 0.0391104783 | H | 1.0699065754 | 5.8365618083 | 1.6295312664 |
| C | 1.0371378587 | 4.8438472306 | -3.7002559967 | H | 0.1233368828 | 4.3094716091 | -3.9905518721 |
| C | -1.0096839222 | 4.2706021223 | 1.0376330214 | H | -1.7960119355 | 3.7687332057 | 0.4574098434 |
| C | 1.1305535471 | 6.1254141186 | -4.540738558 | H | 1.0762553532 | 5.8823658862 | -5.6145285383 |
| C | 2.2190189457 | 3.9194843195 | -4.0302319887 | H | 2.0870874752 | 6.6479196091 | -4.3770435444 |
| C | -0.3205055011 | 3.191753042 | 1.8860316266 | H | 0.3236403855 | 6.837157748 | -4.3139514963 |
| C | -1.6647410509 | 5.3095019794 | 1.9575017345 | H | 2.2326292604 | 3.6887028228 | -5.1081511134 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 2.159539326 | 2.9711332824 | -3.4795316177 | H | 0.0894492434 | 2.3884703503 | 1.2588576823 |
| H | 3.1815151261 | 4.3970003558 | -3.7824082515 | H | -2.1331358825 | 6.1323283772 | 1.39871888 |
| H | -1.0389796324 | 2.7383147769 | 2.5889347887 | H | -0.9308573881 | 5.755904573 | 2.6482509232 |
| H | 0.5043602714 | 3.6149383217 | 2.4824202896 | H | -2.442398192 | 4.8350590698 | 2.5780639292 |

Coordinates of Optimized Structures of $[Fc\text{-}cAAC]^+$ (VIIb)

E° = -2484.1780585; G° = -2483.606488; $E°_{(THF)}$ = -2484.249523

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.185657167 | -1.973234117 | -0.7774144141 | H | -0.5057120731 | 0.1638414148 | -3.8229534258 |
| C | -1.1536198954 | -0.2628772682 | 0.4277540419 | H | 1.2729455898 | 2.6027127367 | -0.6150194617 |
| C | 0.1731388424 | -0.4414352041 | 0.910024264 | H | 2.9614164786 | 0.6215469601 | -1.2159018985 |
| C | 0.7750033099 | -1.4934955826 | 0.1600683442 | H | 1.8769341848 | -0.8595263704 | -3.2064851282 |
| C | 0.1580678967 | 0.5549072706 | -3.0574068899 | H | -2.29889824 | -1.3492872601 | -1.1782832665 |
| C | -0.0557945588 | 1.7428828625 | -2.2417114399 | H | -3.9796975723 | 5.9286390776 | -1.5681278978 |
| C | 1.0995612785 | 1.8424403303 | -1.3696981605 | H | -2.3924421134 | 6.2278722398 | -0.8376375672 |
| C | 2.0036968294 | 0.8048627388 | -1.7018902477 | H | -3.349803459 | 4.7870278171 | -0.3696948341 |
| C | 1.4323136763 | 0.0227753671 | -2.7473070071 | H | -4.0213101156 | 3.7989723866 | -3.6266228206 |
| Fe | 0.2035831889 | 0.0173002574 | -1.1023526618 | H | -3.9865854614 | 3.2070011953 | -1.9596222977 |
| C | -1.3771565606 | -1.2129456274 | -0.6157736021 | H | -3.095574077 | 6.1837114372 | -3.7483066562 |
| C | -1.165651064 | 2.6572124774 | -2.4007172319 | H | -1.7697703474 | 5.2064013425 | -4.4023147435 |
| N | -1.1837951841 | 3.9115423228 | -1.9776646683 | H | -1.4457898284 | 6.4372790093 | -3.1520723921 |
| C | -0.0697911732 | 4.624667571 | -1.3739073535 | H | -4.0981952358 | 0.9685786418 | -3.2898785143 |
| C | -2.4521514116 | 4.6680889411 | -2.3688515613 | H | -3.2521184909 | 0.9328813504 | -1.7263711026 |
| C | -3.0638701242 | 5.438992172 | -1.2043421976 | H | -2.5419188589 | 0.131337574 | -3.150053377 |
| C | -3.3504851052 | 3.5093437775 | -2.8058638945 | H | -3.0878763227 | 2.2525852752 | -5.2583209888 |
| C | -2.1579576097 | 5.6712356861 | -3.4879850336 | H | -1.4977975628 | 1.5039749872 | -5.0207112367 |
| C | -2.4349457829 | 2.3340333671 | -3.1962954045 | H | -1.6481568293 | 3.2688851695 | -5.0442487001 |
| C | -3.1062381107 | 1.0098737961 | -2.8134976999 | H | 2.7894198154 | 6.2579045798 | -2.2436976607 |
| C | -2.1359198806 | 2.342252522 | -4.7130445218 | H | 2.8202362536 | 6.6957590522 | 0.189564599 |
| C | 0.9607702975 | 5.1201996535 | -2.2165057613 | H | 1.049903245 | 5.7552757965 | 1.6372509772 |
| C | 1.9863530025 | 5.8626757415 | -1.6172473518 | H | 0.1560338256 | 4.3404004152 | -4.0424574879 |
| C | 2.0112117323 | 6.106123057 | -0.2493689698 | H | -1.8236804162 | 3.7079489742 | 0.444984999 |
| C | 1.0099209167 | 5.581647752 | 0.5593588323 | H | 1.1212248576 | 5.94335659 | -5.6073180671 |
| C | -0.0448178814 | 4.8262363349 | 0.0300853056 | H | 2.1254062482 | 6.6780881864 | -4.3492150943 |
| C | 1.0651112705 | 4.8653054442 | -3.717280246 | H | 0.3644611969 | 6.8774837757 | -4.2949830426 |
| C | -1.0341198537 | 4.2154035371 | 1.0190551283 | H | 2.2862515005 | 3.7497075978 | -5.1329974288 |
| C | 1.1680117583 | 6.1648179341 | -4.529532412 | H | 2.1951688957 | 2.9866040821 | -3.5270900303 |
| C | 2.2546269593 | 3.9505853017 | -4.0504259777 | H | 3.2107975763 | 4.4237192824 | -3.7762678564 |
| C | -0.3537254831 | 3.1451868223 | 1.8859609418 | H | -1.0827304333 | 2.6944720845 | 2.5784081837 |
| C | -1.6938659009 | 5.263156594 | 1.9276146688 | H | 0.4543498687 | 3.5776778157 | 2.49647569 |
| H | -0.0255054368 | -2.7669676116 | -1.5070666413 | H | 0.0766183532 | 2.3407136088 | 1.2749322238 |
| H | -1.8721070622 | 0.47016359 | 0.7937016363 | H | -2.1409083856 | 6.0953373274 | 1.3666539082 |
| H | 0.653929993 | 0.1299038549 | 1.7029525025 | H | -0.9664504441 | 5.6957099212 | 2.6321220965 |
| H | 1.7958624439 | -1.857582671 | 0.2738475518 | H | -2.4865777727 | 4.7960749301 | 2.5328304326 |

Coordinates of Optimized Structures of $TS_{Nuc}$ (Ib → IVb)

E° = -2484.6882323; G° = -2484.116857; ν = -69.06; $E°_{(THF)}$ = -2484.7592955

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.4957592775 | 2.1630430269 | 1.7501660316 | C | -3.490424525 | 2.513580931 | -0.2967037742 |
| C | -3.7950644882 | 1.5208999862 | 0.6837445031 | C | -4.0053412873 | 3.7605769806 | 0.1718376018 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.6410641004 | 3.5370390325 | 1.4219140742 | C | 1.8955679467 | -2.7865795637 | 2.1266355026 |
| Fe | -2.5576953071 | 2.971990832 | 1.4981363461 | C | -0.1338373878 | -1.4580336491 | 1.4786363641 |
| C | -1.3643693936 | 4.4152577795 | 2.3012464514 | C | 4.9031258606 | 0.8970562009 | 3.8943491621 |
| C | -1.6611276678 | 3.4142133266 | 3.2731385792 | H | 5.2094984456 | 2.1334681794 | 1.0215241157 |
| C | -1.1422039317 | 2.172294938 | 2.793047622 | H | 4.8989887029 | 3.0544548889 | 2.49868578 |
| C | -0.3846478146 | 2.4228831365 | 1.6006000312 | H | 1.9263885838 | 2.8421152727 | -0.592284252 |
| C | -0.6682761767 | 3.7800128762 | 1.2265023273 | H | 2.9702562053 | 1.4122123432 | -0.4201895104 |
| H | -4.8535389289 | 1.6831745737 | 2.6614032417 | H | 3.6779620271 | 2.9846232066 | -0.8531189992 |
| H | -3.5485306902 | 0.4606612979 | 0.6291386651 | H | 0.0396489622 | -2.3449272753 | 4.2677819412 |
| H | -2.9676924267 | 2.3524590191 | -1.2395147118 | H | -0.1514339058 | -1.3863457843 | 6.5402713976 |
| H | -3.9210665914 | 4.7202359698 | -0.3386568896 | H | 0.9076275649 | 0.7919193838 | 7.0560710441 |
| H | -5.1080850043 | 4.2983937952 | 2.0473040871 | H | 2.0620811824 | 4.7605512461 | 1.0374580032 |
| H | -1.6406775181 | 5.4686193225 | 2.3535762064 | H | 3.831734288 | 4.8748817267 | 0.8753615291 |
| H | -2.2044450513 | 3.5626289229 | 4.2063485553 | H | 3.094516663 | 4.6657361458 | 2.4821749886 |
| H | -1.2154087119 | 1.212223976 | 3.3032797997 | H | 4.1001596546 | -1.1421381012 | 2.276771533 |
| H | -0.0814047304 | 1.6521910614 | 0.8974725849 | H | 5.472758773 | -0.3013863507 | 1.5394491613 |
| H | -0.3346029996 | 4.2688373907 | 0.3115678811 | H | 3.8750052847 | -0.2040422789 | 0.7738648668 |
| C | 4.4640681447 | 2.3133276464 | 1.81006932 | H | 3.0072179638 | 2.7391511227 | 4.6658963683 |
| C | 4.1364161055 | 1.0247960806 | 2.5818170352 | H | 3.6455694622 | 3.341466314 | 6.9373775587 |
| N | 2.6252791384 | 1.2286779055 | 2.8017885914 | H | 2.5017287227 | 2.1924823228 | 7.6471989193 |
| C | 2.0646336902 | 2.1604822921 | 2.0843683737 | H | 3.9098528696 | 1.5898630608 | 6.7493533021 |
| C | 3.1221665249 | 2.852456248 | 1.2473930344 | H | 0.4833832415 | 3.2355087968 | 6.3261268072 |
| C | 2.9085074848 | 2.4951999119 | -0.2353192244 | H | 0.7020476683 | 3.5921202216 | 4.5930828997 |
| C | 1.8725682339 | 0.4877442532 | 3.8006928079 | H | 1.6583244013 | 4.4688664148 | 5.814515538 |
| C | 1.2466416679 | -0.7398365336 | 3.4793481986 | H | 1.879661761 | -0.7511488675 | 1.4395173167 |
| C | 0.5250904685 | -1.391249718 | 4.49071978 | H | 2.8833479795 | -2.7949152338 | 2.6107679917 |
| C | 0.4110749226 | -0.8547005988 | 5.7680834116 | H | 1.2596887321 | -3.49786819 | 2.6769568403 |
| C | 1.0128177973 | 0.3662131538 | 6.055190456 | H | 2.0150385073 | -3.1785899432 | 1.10421116 |
| C | 1.7485623581 | 1.0645136776 | 5.0897375684 | H | -0.0823129209 | -1.876691761 | 0.4606910679 |
| C | 3.0168891705 | 4.3743683603 | 1.4231768337 | H | -0.6105152138 | -0.4685771617 | 1.4136008082 |
| C | 4.3935922825 | -0.2289688244 | 1.7426714902 | H | -0.801279533 | -2.1082809936 | 2.0663066651 |
| C | 2.328320708 | 2.4229520487 | 5.4692670368 | H | 4.5520713454 | 0.0411080836 | 4.4905137203 |
| C | 3.1410365314 | 2.3768483554 | 6.7695674126 | H | 4.8414536646 | 1.80480317 | 4.5079730068 |
| C | 1.2275350002 | 3.4888037888 | 5.5535115548 | H | 5.966412258 | 0.7271778838 | 3.6663499017 |
| C | 1.2699676323 | -1.3841300541 | 2.0982176058 | | | | |

Coordinates of Optimized Structures of $TS_{Dep}$ (Ib → IIIb)

E° = -2484.6795216; G° = -2484.113272; ν = -1116.63; $E°_{(THF)}$ = -2484.7268614

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.4591885555 | 2.7316048842 | 1.4703091138 | H | -4.8769367917 | 0.5667751967 | 1.0280714903 |
| C | -4.4794743632 | 1.5281058745 | 0.7035332481 | H | -3.6956150108 | 1.0692057195 | -1.3431245344 |
| C | -3.8705187436 | 1.7975649598 | -0.5512741077 | H | -2.9439972909 | 3.6603864916 | -1.3844957586 |
| C | -3.4611764918 | 3.1569436558 | -0.567591772 | H | -3.6591017444 | 4.778600676 | 0.9752938176 |
| C | -3.8264117105 | 3.7425706693 | 0.6809773085 | H | -0.785583934 | 4.0527017238 | 2.258861924 |
| Fe | -2.5056538942 | 2.1919105473 | 1.0589466217 | H | -2.0036934801 | 2.1917808543 | 3.818889551 |
| C | -0.8925352413 | 2.9911071678 | 2.0300053452 | H | -1.8861796269 | -0.1693736329 | 2.5196748138 |
| C | -1.5329442528 | 2.0110694294 | 2.851133245 | H | 0.0584966158 | 2.8161368373 | 0.0194909257 |
| C | -1.4494432706 | 0.7632622252 | 2.1545014742 | C | 1.9452585581 | -2.0033960062 | -2.3888301537 |
| C | -0.769067492 | 0.9178420558 | 0.9009737407 | C | 1.4998833702 | -3.1066553766 | -1.4093236699 |
| C | -0.4373407873 | 2.3134968873 | 0.8539242261 | N | 0.700761695 | -2.2676822159 | -0.4012178911 |
| H | -4.8634331783 | 2.8577828525 | 2.4745770512 | C | 0.4411211679 | -1.0532894858 | -0.7761683679 |

| | | | |
|---|---|---|---|
| C | 1.0387848868 | -0.7737411914 | -2.1301163542 |
| C | -0.1134381014 | -0.6485382832 | -3.1474493321 |
| C | 0.2325119691 | -2.8065373307 | 0.8648701165 |
| C | -1.0590607169 | -3.3785611632 | 0.9375394304 |
| C | -1.4588939772 | -3.9273784863 | 2.1632890052 |
| C | -0.6287740765 | -3.8947565578 | 3.2789121602 |
| C | 0.6137044973 | -3.2753055576 | 3.1964058881 |
| C | 1.0720409188 | -2.7096355772 | 1.9994786757 |
| C | 1.8373837231 | 0.5380496278 | -2.1052222644 |
| C | 0.5966525291 | -4.153211439 | -2.066133578 |
| C | 2.3952488271 | -1.9538927928 | 2.0135103146 |
| C | 3.5489142825 | -2.778294051 | 2.5980884779 |
| C | 2.2465879038 | -0.6213030289 | 2.7636850199 |
| C | -2.0637501089 | -3.3459184106 | -0.2075143841 |
| C | -2.7058425954 | -4.7096106398 | -0.4870444455 |
| C | -3.1377200284 | -2.2791301616 | 0.0540181095 |
| C | 2.6755682571 | -3.8234129475 | -0.7531214085 |
| H | 2.9942567337 | -1.7364621144 | -2.1889985899 |
| H | 1.8966149189 | -2.3483295074 | -3.4317958401 |
| H | -0.7907490381 | 0.1759226383 | -2.8765411481 |
| H | -0.7114788741 | -1.5692773266 | -3.2189979377 |
| H | 0.296649713 | -0.4349534907 | -4.1470979394 |
| H | -2.4479030693 | -4.3845797968 | 2.2461125858 |
| H | -0.9592820043 | -4.3381456759 | 4.2219844414 |
| H | 1.2442896208 | -3.2204408999 | 4.0870061754 |
| H | 1.1829266578 | 1.4014380632 | -1.9125839467 |
| H | 2.3270726299 | 0.6974705984 | -3.0789778953 |
| H | 2.6216964827 | 0.5239567922 | -1.332447658 |
| H | 0.1925427272 | -4.8586580546 | -1.3259530354 |
| H | 1.196316942 | -4.7349118191 | -2.7820793197 |
| H | -0.2385897507 | -3.706143775 | -2.6226483517 |
| H | 2.6569135032 | -1.7040821953 | 0.9754322136 |
| H | 4.4992665728 | -2.2317315841 | 2.4929273008 |
| H | 3.4078724704 | -2.9721781751 | 3.6728967682 |
| H | 3.6598469601 | -3.752265346 | 2.098519905 |
| H | 1.9905562679 | -0.7859190235 | 3.8226436027 |
| H | 1.45790361 | 0.0063692739 | 2.3229930156 |
| H | 3.1916606365 | -0.0556881228 | 2.7340504286 |
| H | -1.533737898 | -3.0389777107 | -1.1180351474 |
| H | -1.9533984226 | -5.4951649368 | -0.6541311918 |
| H | -3.3487556744 | -5.0396956022 | 0.3438538181 |
| H | -3.342532757 | -4.6555221339 | -1.384220793 |
| H | -3.8428636728 | -2.2293059283 | -0.7918416512 |
| H | -2.6875054614 | -1.2835556396 | 0.189800842 |
| H | -3.7204502213 | -2.5152873988 | 0.9593134313 |
| H | 2.3421159386 | -4.5305703245 | 0.0211188448 |
| H | 3.400170718 | -3.126681931 | -0.3122686673 |
| H | 3.2043316824 | -4.4033270354 | -1.5246261315 |
| H | -0.2327656791 | -0.1449928179 | -0.0148792019 |

**Molecular orbital diagram of 1a and 1b**

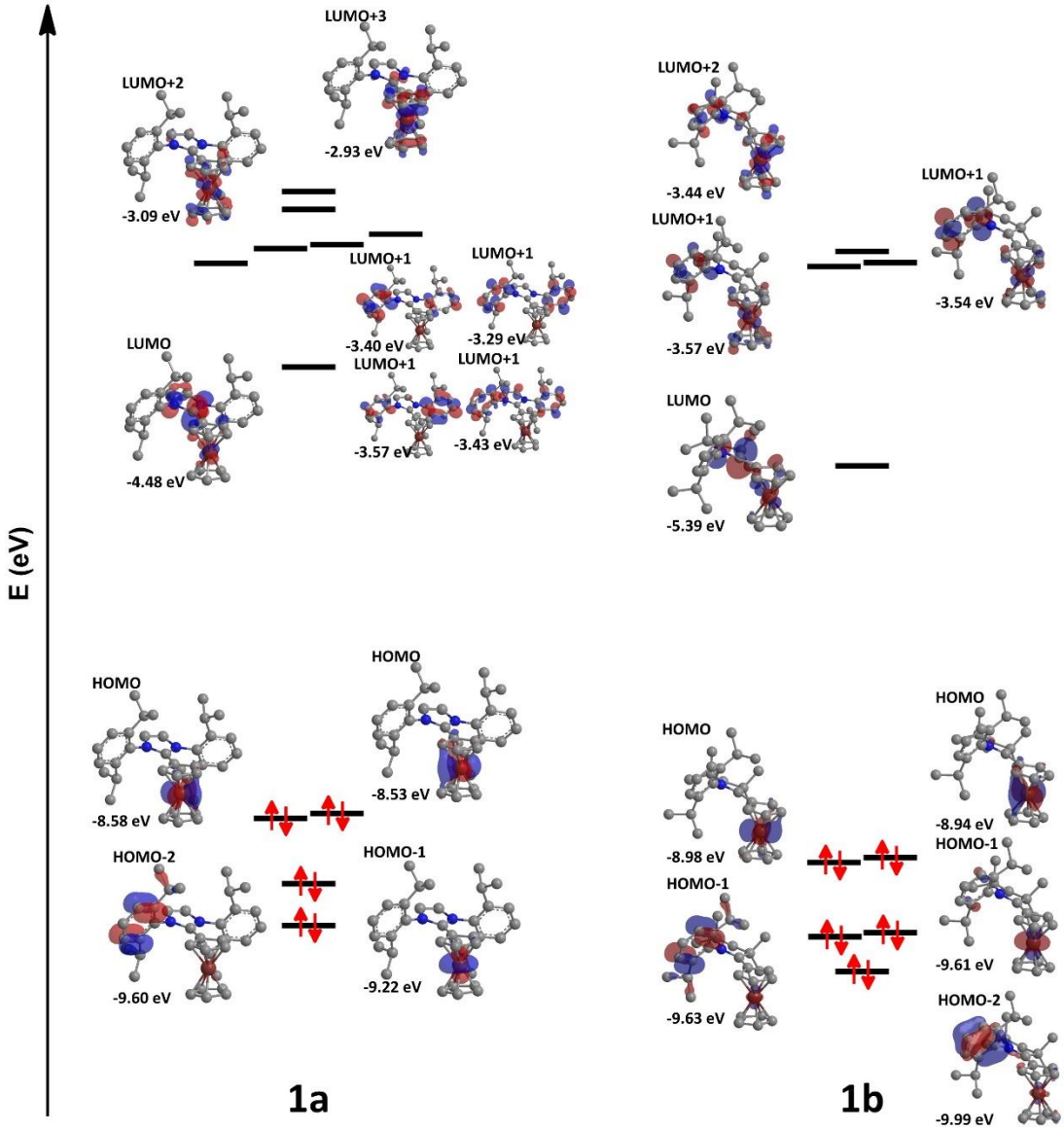



**Figure S4**. Molecular orbital diagram of **1a** and **1b**

**Spin Density of [Fc-NHC] radical (2a and 2b)**

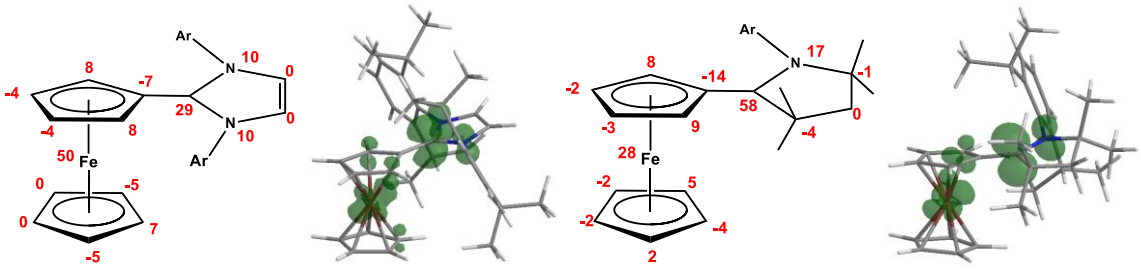



**Figure S5**. Spin densities and the visualization of **2a** and **2b**

**TD-DFT of 1a,1b, 2a, and 2b**

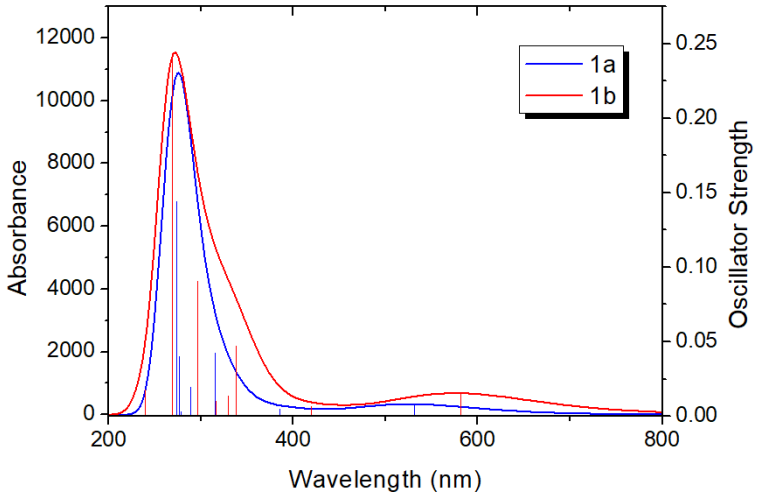



**Figure S6**. Simultated UV-Vis spectra and oscillator strengths of **1a** and **1b**

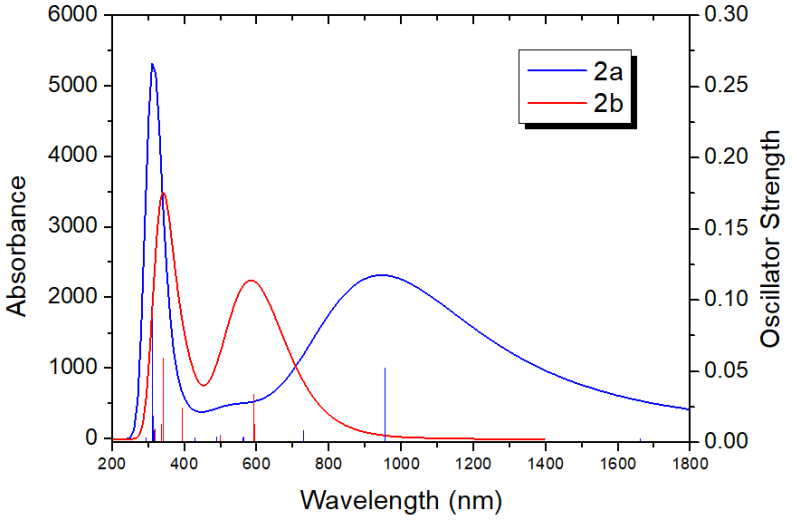



**Figure S7**. Simultated UV-Vis-NIR spectra and oscillator strengths of **2a** and **2b**

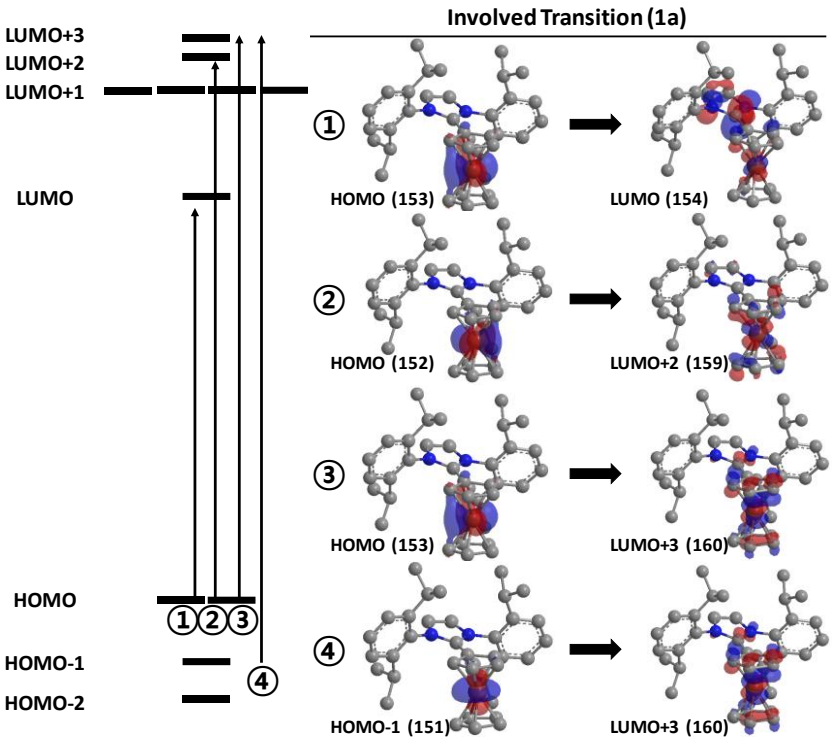



**Figure S8**. Simplified scheme of electron transition and their involved orbital transitions of **1a** in TD-DFT calculation

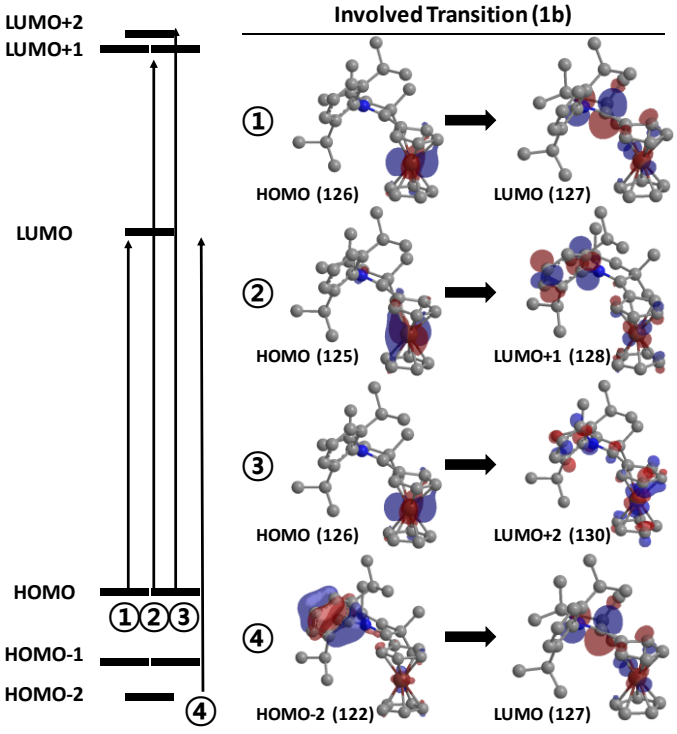



**Figure S9**. Simplified scheme of electron transition and their involved orbital transitions of **1b** in TD-DFT calculation

**Major transition of 1a**

Excited State 2: 2.3326 eV 531.53 nm f=0.0071
<S**2>=0.000
152 ->159 -0.25747
153 ->154 0.48284
153 ->160 -0.37927
.
Excited State 5: 3.2146 eV 385.69 nm f=0.0050
<S**2>=0.000
151 ->154 0.31336
151 ->160 -0.14289
152 ->156 -0.13446
152 ->159 0.46666
153 ->154 0.34164

Excited State 8: 3.9348 eV 315.10 nm f=0.0422
<S**2>=0.000
151 ->154 -0.14105
152 ->159 -0.12569
153 ->154 0.32708
153 ->155 0.16333
153 ->160 0.53096

Excited State 9: 4.2960 eV 288.60 nm f=0.0197
<S**2>=0.000
144 ->154 -0.11629
148 ->160 0.10247
151 ->154 0.41904
151 ->160 0.49165

Excited State 13: 4.4811 eV 276.68 nm f=0.0400
<S**2>=0.000
147 ->154 0.14910
149 ->154 0.54979
150 ->154 -0.37890

Excited State 14: 4.5263 eV 273.92 nm f=0.1441
<S**2>=0.000
147 ->154 0.29379
148 ->154 0.54867
149 ->154 -0.15445
150 ->154 -0.19590
151 ->160 0.12267

Excited State 15: 4.5408 eV 273.05 nm f=0.0417
<S**2>=0.000
147 ->154 0.44863
148 ->154 -0.37032
149 ->154 -0.29381
150 ->154 -0.18887
153 ->156 -0.12698

## Major Transition of 1b

Excited State 2: 2.1328 eV 581.32 nm f=0.0150
<S**2>=0.000
125 ->128 0.17156
126 ->127 0.54777
126 ->129 -0.17690
126 ->130 0.29677
126 ->131 -0.11173

Excited State 5: 2.9571 eV 419.28 nm f=0.0064
<S**2>=0.000
124 ->127 0.24408
125 ->128 0.44674
125 ->129 -0.25981
125 ->130 -0.12863
125 ->131 -0.11165
126 ->127 -0.31234
126 ->129 -0.11428

Excited State 8: 3.6696 eV 337.87 nm f=0.0470
<S**2>=0.000
123 ->127 -0.11656
124 ->127 -0.22980
124 ->128 -0.11937
124 ->130 0.13938
125 ->129 0.17080
125 ->130 -0.16808
126 ->127 -0.24415
126 ->128 -0.19732
126 ->129 -0.14213
126 ->130 0.40633

Excited State 10: 3.7631 eV 329.47 nm f=0.0135
<S**2>=0.000
122 ->127 0.66573
124 ->127 -0.11809

Excited State 11: 3.9170 eV 316.53 nm f=0.0100
<S**2>=0.000
119 ->127 0.10334
120 ->127 -0.13287
121 ->127 0.41406
123 ->130 0.10620
124 ->127 -0.22792
124 ->129 -0.14546
124 ->130 0.32066
125 ->128 0.11688
126 ->130 -0.15522

Excited State 13: 4.1807 eV 296.56 nm f=0.0909 <S**2>=0.000
120 ->127 0.63410
121 ->127 -0.10159
124 ->130 0.19067

Excited State 15: 4.6167 eV 268.55 nm f=0.2438 <S**2>=0.000
118 ->127 0.15854
119 ->127 0.64763

Excited State 20: 5.1748 eV 239.59 nm f=0.0176 <S**2>=0.000
122 ->129 0.11765
122 ->131 -0.32445
123 ->128 0.30811
123 ->129 0.35808
123 ->130 0.19492
124 ->129 -0.15811
125 ->131 0.19859

## Major Transition of 2a

Excited State 1: 0.7469 eV 1660.06 nm f=0.0032 <S**2>=0.830
154A ->155A 0.98990

Excited State 6: 1.2978 eV 955.33 nm f=0.0525 <S**2>=0.744
152A ->159A -0.15083
154A ->159A 0.95417
153B ->158B -0.14850

Excited State 7: 1.7030 eV 728.03 nm f=0.0087 <S**2>=0.917
154A ->156A -0.10171
154A ->160A 0.17809
154A ->161A 0.96341
150B ->159B 0.10229

Excited State 11: 2.1981 eV 564.06 nm f=0.0041 <S**2>=1.970
151A ->160A -0.19031
152A ->159A -0.36757
152A ->160A 0.17144
153A ->159A 0.18296
153A ->160A 0.13524
150B ->162B 0.11467
151B ->158B 0.14908
151B ->160B 0.16405
151B ->162B -0.20598
152B ->158B 0.28157
152B ->161B 0.13016
152B ->162B -0.36519
153B ->158B -0.29367
153B ->160B -0.14606
153B ->161B -0.15329
153B ->162B 0.44618

Excited State 12: 2.2101 eV 561.00 nm f=0.0037 <S**2>=2.032
151A ->160A 0.24703
152A ->159A -0.13813
152A ->160A -0.28385
153A ->159A -0.37498
151B ->158B 0.10598
151B ->160B -0.19103
151B ->162B -0.15459
152B ->158B -0.26633
152B ->161B -0.11620
152B ->162B 0.33763
153B ->158B -0.29557
153B ->160B 0.16361
153B ->161B -0.16326
153B ->162B 0.44823

Excited State 14: 2.5327 eV 489.53 nm f=0.0043 <S**2>=0.835
154A ->162A 0.97034
154A ->163A 0.15444
154A ->166A -0.13097

Excited State 19: 2.8994 eV 427.62 nm f=0.0034 <S**2>=0.835
154A ->162A -0.15689
154A ->163A 0.96679
154A ->164A 0.10756

Excited State 37: 3.6295 eV 341.60 nm f=0.0038 <S**2>=1.625
152A ->155A 0.58606
153A ->155A 0.55323
154A ->168A 0.12107
154A ->170A 0.21782
154A ->171A 0.34608
154A ->173A -0.11243
153B ->158B 0.19918
153B ->162B 0.16048

Excited State 49: 3.8853 eV 319.11 nm f=0.0036 <S**2>=0.897

154A ->168A -0.27045
154A ->169A 0.42396
154A ->170A 0.64194
154A ->171A -0.40919
154A ->172A 0.10974
154A ->174A -0.15124
152B ->158B -0.13070
152B ->162B -0.19036

Excited State 50: 3.9191 eV 316.36 nm f=0.0089 <S**2>=1.590
152A ->159A -0.14658
154A ->170A 0.10277
151B ->154B 0.84104
151B ->156B 0.13620
151B ->158B 0.16622
153B ->158B -0.21756
153B ->161B 0.10035
153B ->162B -0.25778

Excited State 51: 3.9578 eV 313.27 nm f=0.0183 <S**2>=1.065
151A ->155A 0.10079
151A ->159A 0.19715
152A ->159A 0.28999
153A ->156A -0.13578
153A ->160A -0.15946
154A ->174A -0.20608
151B ->154B 0.48355
151B ->158B -0.20506
152B ->160B -0.15225
153B ->158B 0.33518
153B ->161B -0.17525
153B ->162B 0.44618

Excited State 52: 3.9872 eV 310.96 nm f=0.0869 <S**2>=0.892
152A ->159A 0.10795
154A ->173A 0.26297
154A ->174A 0.66920
154A ->175A -0.14076
154A ->176A 0.15865
154A ->177A 0.29626
154A ->178A -0.12653
154A ->179A -0.27163
154A ->181A -0.19934
154A ->182A 0.10030
153B ->158B 0.21027
153B ->162B 0.14670

Excited State 58: 4.2329 eV 292.91 nm f=0.0034 <S**2>=2.332
142A ->161A -0.19475
148A ->161A 0.12935
150A ->156A 0.18594
150A ->161A 0.32615
151A ->156A 0.24609
152A ->161A -0.16888
154A ->161A 0.13224
142B ->159B -0.18569
150B ->155B -0.22583
150B ->159B -0.37278
151B ->155B 0.10018
153B ->159B 0.57170

## Major Transition of 2b

Excited State 6: 2.0878 eV 593.86 nm f=0.0128 <S**2>=1.566
124A ->130A -0.30725
124A ->131A -0.12848
125A ->130A 0.10963
126A ->131A 0.33415
127A ->128A -0.17684
127A ->130A 0.26105
127A ->131A 0.11395
124B ->127B 0.46240
124B ->128B -0.11001
124B ->130B 0.10563
124B ->131B -0.46480
126B ->127B 0.29890
126B ->131B -0.24325

Excited State 7: 2.0946 eV 591.92 nm f=0.0341 <S**2>=1.073
124A ->131A -0.11804
125A ->130A 0.28693
127A ->128A -0.38694
127A ->130A 0.54440
124B ->127B -0.34344
124B ->130B 0.13640
124B ->131B 0.36712
125B ->130B -0.12774
126B ->127B 0.10501
126B ->131B -0.23477

Excited State 11: 2.4833 eV 499.27 nm f=0.0055 <S**2>=1.845
125A ->128A -0.17968
125A ->130A 0.65125
126A ->131A 0.11168
127A ->129A -0.32243
127A ->130A -0.41272

125B ->130B -0.21994
126B ->127B 0.28275
126B ->131B 0.28120

Excited State 15: 3.1481 eV 393.84 nm f=0.0246
<S**2>=1.214
124A ->128A -0.15151
124A ->130A 0.52634
126A ->131A -0.39413
127A ->130A 0.18312
124B ->127B 0.34503
125B ->130B 0.35182
126B ->127B 0.39524
126B ->131B 0.25206

Excited State 18: 3.6489 eV 339.78 nm f=0.0596
<S**2>=1.005
124A ->130A -0.14261
124A ->131A -0.10099
125A ->128A 0.13135
125A ->130A -0.31106
125A ->131A 0.11615
126A ->130A 0.16064
126A ->131A 0.17303
127A ->130A 0.21079
124B ->127B -0.26821
124B ->130B -0.10454
125B ->127B 0.13552
125B ->130B -0.18105
125B ->131B 0.28676
126B ->127B 0.35707
126B ->128B 0.27727
126B ->131B 0.50430

Excited State 19: 3.6757 eV 337.31 nm f=0.0134
<S**2>=0.955
124A ->131A -0.21129
125A ->130A 0.17479
125A ->131A 0.26113
126A ->128A -0.11212
126A ->130A 0.28174
124B ->130B -0.23403
125B ->127B 0.30640
125B ->128B 0.12632
125B ->131B 0.59539
126B ->127B -0.16236
126B ->128B -0.12674
126B ->130B 0.23277
126B ->131B -0.24817

Excited State 20: 3.8919 eV 318.57 nm f=0.0099
<S**2>=1.731
125A ->130A 0.10452
127A ->132A 0.11459
124B ->127B 0.11013
126B ->128B 0.89310
126B ->129B -0.18249
126B ->131B -0.28903

## Mössbauer DFT Calculations:

Mössbauer parameters were calculated with ORCA 4.0.1.2 following procedure established in the following reference,[17] using the TPSSh functional and substitution of CPCM flag for COSMO. All geometries were optimized with the TPSSh functional using an ORCA example input file described in the reference. All Mössbauer single-point calculations (TPSSh functional) used an input file described in the reference. Parameters α, β, and C in the equation $\delta_{IS}=\alpha(\rho-C)+\beta$ were fitted to experimental isomer shifts and computed electron densities for molecules (α = -0.176832008, C = 23600, β = 0.359641078).

**Table S3.** Computed electron densities ρ and Mössbauer isomer shift and quadrupole splitting parameters with experimental data.

| | $\rho$ | Calc $\delta_{IS}$ | Calc $\Delta E_Q$ | Expt $\delta_{IS}$ | Expt $\Delta E_Q$ | \|Diff $\delta_{IS}$\| | \|Diff $\Delta E_Q$\| |
|---|---|---|---|---|---|---|---|
| **1a** | 23599.056824968 | 0.526 | 2.366 | 0.528 | 2.266 | 0.002 | 0.100 |
| **2a** | 23598.618341977 | 0.604 | 1.895 | 0.644 | 1.710 | 0.040 | 0.185 |
| **1b** | 23599.091493203 | 0.520 | 2.290 | 0.539 | 2.215 | 0.019 | 0.075 |
| **2b** | 23598.774644565 | 0.576 | 2.092 | 0.592 | 1.924 | 0.016 | 0.168 |
| **$Fe(C_5H_5)_2^+$** | 23599.123336072 | 0.515 | 0.465 | 0.543 | 0.353 | 0.028 | 0.112 |
| **$Fe(C_5H_5)_2$** | 23598.94963868 | 0.545 | 2.592 | 0.539 | 2.434 | 0.006 | 0.158 |

Coordinates of Optimized Structures of **1a** with TPSSh level of theory

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fe | -2.313878203 | 1.582117679 | 0.656136679 | H | -3.119644138 | -0.584673556 | -0.940092511 |
| N | 0.392273395 | -1.388459668 | 0.340272958 | H | -3.294532833 | 1.900125027 | -1.960645195 |
| N | 0.94712005 | -0.030061842 | -1.254132307 | H | -4.195207086 | 3.537547477 | -0.026522908 |
| C | -4.260366024 | 1.691389326 | 1.23787267 | H | 2.096880783 | -1.404391198 | -2.441278363 |
| C | -3.904174532 | 0.342468238 | 0.942003595 | H | 1.384621546 | -3.144958368 | -0.40191405 |
| C | -3.476538945 | 0.289933378 | -0.417855779 | H | -1.34333298 | 4.184488197 | 1.02873179 |
| C | -3.564389282 | 1.604903638 | -0.960210141 | H | -1.755461973 | 2.626857439 | 3.192458343 |
| C | -4.049022061 | 2.471334272 | 0.063031276 | H | -0.954320154 | 0.152247005 | 2.612472314 |
| C | 1.49710789 | -1.263604331 | -1.559843221 | H | -0.270926677 | 2.688712186 | -0.894078274 |
| C | 1.1536554 | -2.108018936 | -0.567279238 | H | -2.409216525 | -4.167558738 | 2.676366307 |
| C | 0.26738228 | -0.103518393 | -0.081433149 | H | -1.25271827 | -3.691604255 | 4.794645447 |
| C | 1.317428703 | 1.164967124 | -1.978281378 | H | 0.678054506 | -2.163233976 | 4.848374987 |
| C | -1.084900305 | 3.140638387 | 1.121675071 | H | 0.38485738 | 3.058347074 | -4.605824095 |
| C | -1.302754579 | 2.318813345 | 2.262339642 | H | 2.372915103 | 4.312943455 | -3.880385975 |
| C | -0.885718927 | 0.998847174 | 1.952680122 | H | 3.696135202 | 3.554539057 | -1.943309031 |
| C | -0.367645842 | 0.998508047 | 0.603139435 | H | 2.850042256 | 0.458310089 | 0.024704347 |
| C | -0.527859944 | 2.341678178 | 0.091254165 | H | 5.289573712 | 0.680623996 | 0.068967031 |
| C | -0.086346433 | -1.988457821 | 1.566515488 | H | 4.738989851 | 0.298113263 | -1.572542789 |
| C | -1.164652043 | -2.87711901 | 1.494383328 | H | 5.230213948 | 1.949977715 | -1.165804522 |
| C | -1.57283888 | -3.478537017 | 2.68679523 | H | 3.821851433 | 2.04431764 | 1.630259621 |
| C | -0.918421055 | -3.214570619 | 3.880027812 | H | 2.233418332 | 2.622237985 | 1.09275354 |
| C | 0.169416815 | -2.349326499 | 3.910208064 | H | 3.709017083 | 3.35867037 | 0.449040956 |
| C | 0.614711302 | -1.716989576 | 2.751515233 | H | -1.098362223 | 0.290394947 | -2.631911192 |
| C | 0.546660168 | 1.55881602 | -3.077582692 | H | -2.664024127 | 1.074865183 | -4.288694153 |
| C | 0.953825583 | 2.708660029 | -3.753048903 | H | -1.975627943 | 2.517649838 | -3.516429118 |
| C | 2.077323378 | 3.418691575 | -3.343202748 | H | -1.43703765 | 2.027212143 | -5.12586191 |
| C | 2.821432864 | 2.992903215 | -2.252395427 | H | -1.145120208 | -0.906633481 | -4.816999777 |
| C | 2.459275703 | 1.845103992 | -1.546075807 | H | 0.444483118 | -1.042654809 | -4.052605532 |
| C | 3.285252863 | 1.382822299 | -0.361886699 | H | 0.20524706 | 0.092667402 | -5.388972257 |
| C | 4.724098984 | 1.057961587 | -0.787184379 | H | 1.71065483 | -0.06695292 | 1.975184372 |
| C | 3.257286717 | 2.416923056 | 0.771381931 | H | 3.972247266 | -0.917382813 | 2.50678543 |
| C | -0.669472198 | 0.767921049 | -3.519663267 | H | 3.265460883 | -2.343562301 | 3.286985469 |
| C | -1.749000805 | 1.65467446 | -4.146602279 | H | 3.076539116 | -2.104497264 | 1.543103395 |
| C | -0.262595242 | -0.343524854 | -4.501918662 | H | 2.188413094 | -0.662230377 | 4.92668272 |
| C | 1.824034976 | -0.798799577 | 2.778526185 | H | 1.022709108 | 0.525558753 | 4.316123069 |
| C | 3.11211866 | -1.592678884 | 2.507523732 | H | 2.752801115 | 0.722652863 | 3.991624004 |
| C | 1.946749269 | -0.009200215 | 4.084608625 | H | -1.576686064 | -2.495358795 | -0.563278456 |
| C | -1.833991409 | -3.250145585 | 0.185003054 | H | -0.225524565 | -4.624219653 | -0.417787708 |
| C | -1.311211336 | -4.611840163 | -0.306136809 | H | -1.585458117 | -5.39402678 | 0.407312939 |
| C | -3.361067375 | -3.31173654 | 0.292491813 | H | -1.759506367 | -4.85501922 | -1.272856054 |
| H | -4.590408824 | 2.064064226 | 2.196026212 | H | -3.789917521 | -3.470890008 | -0.699605284 |
| H | -3.926012497 | -0.478849871 | 1.641522167 | H | -3.778388284 | -2.394184854 | 0.706583237 |

| | | | |
|---|---|---|---|
| H | -3.677967276 | -4.143701628 | 0.925996235 |

Coordinates of Optimized Structures of **2a** with TPSSh level of theory

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fe | -2.446098326 | 1.671188504 | 0.637276432 | H | -3.268537275 | -0.403948876 | -1.08858197 |
| N | 0.374941752 | -1.442106357 | 0.346162538 | H | -3.29468701 | 2.136897697 | -2.002021378 |
| N | 0.86925284 | -0.053970648 | -1.31055634 | H | -4.269306466 | 3.72483653 | -0.059885685 |
| C | -4.445331893 | 1.835251249 | 1.127385286 | H | 1.890965111 | -1.485441169 | -2.558226715 |
| C | -4.102047312 | 0.487375003 | 0.793831642 | H | 1.251175576 | -3.210058034 | -0.522444338 |
| C | -3.618227867 | 0.464609702 | -0.549667727 | H | -1.328475953 | 4.155381257 | 1.143038063 |
| C | -3.624768565 | 1.808355316 | -1.029154221 | H | -1.892168597 | 2.504768622 | 3.217740519 |
| C | -4.147882133 | 2.652514206 | 0.001860184 | H | -1.174543117 | 0.027264588 | 2.519621837 |
| C | 1.348350256 | -1.319536852 | -1.644315721 | H | -0.263762593 | 2.686414385 | -0.815441402 |
| C | 1.041089854 | -2.162274793 | -0.646438593 | H | -2.100886394 | -4.411803012 | 2.795599863 |
| C | 0.269044879 | -0.102014752 | -0.046059691 | H | -0.894090603 | -3.854612112 | 4.87157631 |
| C | 1.316632777 | 1.129105407 | -1.985193254 | H | 0.886220243 | -2.149251265 | 4.852259393 |
| C | -1.132579388 | 3.093531328 | 1.190989787 | H | 0.560954018 | 3.067030285 | -4.654788525 |
| C | -1.430370533 | 2.225029405 | 2.281554432 | H | 2.527542448 | 4.290756991 | -3.817093017 |
| C | -1.054594517 | 0.902436438 | 1.903088257 | H | 3.73195829 | 3.492867082 | -1.816668929 |
| C | -0.375775932 | 0.946839233 | 0.620291044 | H | 2.745473325 | 0.394699215 | 0.060291289 |
| C | -0.576979132 | 2.304161105 | 0.142016403 | H | 5.199374943 | 0.582653513 | 0.205966224 |
| C | 0.001043163 | -2.048854014 | 1.585112786 | H | 4.700271273 | 0.209940583 | -1.453900238 |
| C | -1.019252031 | -3.012986823 | 1.576415466 | H | 5.201126395 | 1.853819707 | -1.027697339 |
| C | -1.318840241 | -3.660170667 | 2.777026152 | H | 3.699722132 | 1.959238359 | 1.720780626 |
| C | -0.642346985 | -3.347077402 | 3.946438033 | H | 2.130262881 | 2.541901245 | 1.1320545 |
| C | 0.358422207 | -2.380194727 | 3.934044894 | H | 3.632551086 | 3.279196034 | 0.543764186 |
| C | 0.707530265 | -1.720881013 | 2.757724251 | H | -1.032426087 | 0.27951328 | -2.783277612 |
| C | 0.618618068 | 1.560305954 | -3.123376472 | H | -2.574089728 | 1.175012606 | -4.418624564 |
| C | 1.079397301 | 2.70520372 | -3.774231976 | H | -1.88661397 | 2.559605877 | -3.548505995 |
| C | 2.188225387 | 3.3982379 | -3.302123876 | H | -1.326666438 | 2.166550684 | -5.178032891 |
| C | 2.862808039 | 2.950450469 | -2.174729419 | H | -1.052805252 | -0.785953973 | -5.045244346 |
| C | 2.446422391 | 1.801109517 | -1.501406697 | H | 0.520956687 | -0.972887705 | -4.256581449 |
| C | 3.218473257 | 1.311954971 | -0.294050561 | H | 0.310902624 | 0.239342755 | -5.529881677 |
| C | 4.667581795 | 0.969335776 | -0.668038158 | H | 1.639336404 | 0.003106405 | 1.948459565 |
| C | 3.164655705 | 2.337623621 | 0.84551376 | H | 3.98879697 | -0.720024577 | 2.331414951 |
| C | -0.592471524 | 0.80569962 | -3.635623142 | H | 3.408429294 | -2.201483882 | 3.111432172 |
| C | -1.655702855 | 1.736155613 | -4.227893376 | H | 3.095643403 | -1.926295066 | 1.388864523 |
| C | -0.175179461 | -0.245826348 | -4.677932717 | H | 2.344431228 | -0.596902137 | 4.859768737 |
| C | 1.853518364 | -0.727690371 | 2.731653432 | H | 1.075834736 | 0.526217747 | 4.335274324 |
| C | 3.165714025 | -1.439695707 | 2.364825842 | H | 2.769038583 | 0.828359989 | 3.912515316 |
| C | 2.013835581 | 0.048594572 | 4.041322009 | H | -1.543309673 | -2.629096846 | -0.44688244 |
| C | -1.795814529 | -3.363639083 | 0.32132802 | H | -0.345874929 | -4.8417543 | -0.401035921 |
| C | -1.416492811 | -4.75871313 | -0.199944334 | H | -1.683452812 | -5.524213665 | 0.534765883 |
| C | -3.310174989 | -3.300506068 | 0.558418128 | H | -1.957065426 | -4.973000456 | -1.126151861 |
| H | -4.82638638 | 2.174326224 | 2.080159865 | H | -3.841415849 | -3.445662357 | -0.386060555 |
| H | -4.200211906 | -0.362408214 | 1.452550399 | H | -3.60418045 | -2.338277475 | 0.979034017 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -3.634603625 | -4.085531413 | 1.246511786 | | | | |

Coordinates of Optimized Structures of **1b** with TPSSh level of theory

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fe | 0.203345778 | 0.080768516 | -1.123466142 | H | -0.482777212 | 0.211972895 | -3.822724327 |
| N | -1.19741155 | 3.884852844 | -1.931415785 | H | 1.291699936 | 2.61042333 | -0.610732262 |
| C | -0.124793383 | -1.880793797 | -0.713941181 | H | 2.947187587 | 0.603376208 | -1.18584627 |
| C | -1.297662317 | -0.136334417 | 0.240035499 | H | 1.872384776 | -0.848036722 | -3.181354601 |
| C | -0.030495641 | -0.222535681 | 0.886036033 | H | -2.181365227 | -1.36181067 | -1.417259458 |
| C | 0.695653425 | -1.294654906 | 0.293789886 | H | -4.010281353 | 5.821263881 | -1.451661919 |
| C | 0.187105108 | 0.591120169 | -3.071646243 | H | -2.439951726 | 6.081871231 | -0.691802502 |
| C | -0.022825679 | 1.770491671 | -2.248312597 | H | -3.38772318 | 4.61435008 | -0.323152551 |
| C | 1.123317998 | 1.862823091 | -1.365651875 | H | -3.975669255 | 3.789742955 | -3.638905694 |
| C | 2.016110993 | 0.811564367 | -1.690855387 | H | -3.986983435 | 3.129054478 | -1.999528262 |
| C | 1.446877972 | 0.043637405 | -2.746416454 | H | -3.096333134 | 6.204321315 | -3.59860972 |
| C | -1.357951616 | -1.167304319 | -0.748458169 | H | -1.750117763 | 5.282459061 | -4.268891541 |
| C | -1.14843816 | 2.653094601 | -2.393082004 | H | -1.469896775 | 6.433099449 | -2.94522532 |
| C | -0.074617895 | 4.603901449 | -1.355016261 | H | -4.008211431 | 0.958036856 | -3.423024147 |
| C | -2.475198543 | 4.628812197 | -2.301038698 | H | -3.198742467 | 0.851016404 | -1.852882561 |
| C | -3.104648111 | 5.320964178 | -1.102085529 | H | -2.445301621 | 0.150520632 | -3.299582394 |
| C | -3.341566974 | 3.476741067 | -2.809503671 | H | -2.953828665 | 2.234297009 | -5.29026726 |
| C | -2.163957317 | 5.694578348 | -3.350445155 | H | -1.29234461 | 1.692569825 | -5.014007617 |
| C | -2.38929675 | 2.339261854 | -3.218711682 | H | -1.673405051 | 3.415569627 | -4.99899 |
| C | -3.036774694 | 0.983493854 | -2.923418828 | H | 2.792999566 | 6.133594078 | -2.296494741 |
| C | -2.041304341 | 2.427500374 | -4.722309247 | H | 2.872613583 | 6.600787857 | 0.123833827 |
| C | 0.945083412 | 5.053495755 | -2.217852206 | H | 1.107338466 | 5.733560101 | 1.606313372 |
| C | 1.996412889 | 5.775832518 | -1.653509535 | H | 0.092484074 | 4.235667079 | -4.000252663 |
| C | 2.045291193 | 6.037100096 | -0.292462449 | H | -1.780971609 | 3.684477631 | 0.464975465 |
| C | 1.045824591 | 5.55620409 | 0.538256493 | H | 0.979525398 | 5.822417607 | -5.599375237 |
| C | -0.029373772 | 4.823873647 | 0.032645758 | H | 2.032324806 | 6.561661014 | -4.3859786 |
| C | 0.997812512 | 4.769348992 | -3.709604212 | H | 0.279620282 | 6.764004172 | -4.272333228 |
| C | -1.006065895 | 4.212709147 | 1.02228287 | H | 2.190689778 | 3.663058669 | -5.136879869 |
| C | 1.07179816 | 6.062188905 | -4.536795312 | H | 2.156764564 | 2.922235054 | -3.527340883 |
| C | 2.193183663 | 3.870826447 | -4.063446446 | H | 3.133545948 | 4.370786318 | -3.816199268 |
| C | -0.280732242 | 3.17775596 | 1.893664431 | H | -1.000665329 | 2.649786296 | 2.525093684 |
| C | -1.667997002 | 5.256159667 | 1.932363166 | H | 0.45255013 | 3.665454988 | 2.541174004 |
| H | 0.158190275 | -2.689897121 | -1.370976206 | H | 0.240468003 | 2.447008418 | 1.27676528 |
| H | -2.065286425 | 0.595843975 | 0.442923214 | H | -2.195203801 | 6.025682233 | 1.368046354 |
| H | 0.335961341 | 0.424055016 | 1.666715117 | H | -0.91847885 | 5.747543863 | 2.558241717 |
| H | 1.707305745 | -1.584444011 | 0.536028737 | H | -2.383659148 | 4.761088833 | 2.594381265 |

Coordinates of Optimized Structures of **2b** with TPSSh level of theory

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fe | 0.275087848 | -0.000543279 | -1.119731841 | C | -1.291871591 | -0.237165572 | 0.177535461 |
| N | -1.231342473 | 3.905264375 | -1.841433401 | C | -0.047578813 | -0.303593392 | 0.875944795 |
| C | -0.055507679 | -1.981661055 | -0.705746526 | C | 0.709753421 | -1.387541223 | 0.337767167 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.207423634 | 0.578854283 | -3.067510288 | H | 1.929839854 | -0.835784602 | -3.186102889 |
| C | -0.024249782 | 1.7854606 | -2.295496583 | H | -2.079233438 | -1.469823579 | -1.518051611 |
| C | 1.087149021 | 1.846836283 | -1.363864364 | H | -4.069621645 | 5.816936929 | -1.468232126 |
| C | 2.02596728 | 0.819926783 | -1.676873673 | H | -2.527749561 | 6.091085461 | -0.653684505 |
| C | 1.481313992 | 0.039070775 | -2.737444957 | H | -3.459840447 | 4.610135142 | -0.325765728 |
| C | -1.292005422 | -1.269326088 | -0.807038785 | H | -3.968357465 | 3.836523639 | -3.631665262 |
| C | -1.121073059 | 2.660371223 | -2.450261746 | H | -3.958732634 | 3.110058009 | -2.02118852 |
| C | -0.101193274 | 4.629420683 | -1.333153997 | H | -3.092602444 | 6.222233458 | -3.581561339 |
| C | -2.467461864 | 4.638121258 | -2.264566559 | H | -1.72525396 | 5.303946546 | -4.218843293 |
| C | -3.167268662 | 5.324634967 | -1.095751161 | H | -1.477359714 | 6.460065095 | -2.899244162 |
| C | -3.320436026 | 3.494442895 | -2.821767708 | H | -3.983925903 | 0.963700427 | -3.480431165 |
| C | -2.162903948 | 5.715537506 | -3.310625517 | H | -3.179935553 | 0.901812062 | -1.899908805 |
| C | -2.363020466 | 2.374272496 | -3.276119652 | H | -2.409492623 | 0.178779118 | -3.316142081 |
| C | -3.015237342 | 1.017017302 | -2.973090411 | H | -2.991510701 | 2.266061377 | -5.352516434 |
| C | -2.073419097 | 2.460009209 | -4.788495572 | H | -1.326508304 | 1.722333388 | -5.088274836 |
| C | 0.934049831 | 5.052001578 | -2.196911664 | H | -1.701879108 | 3.445838531 | -5.073559407 |
| C | 2.003873635 | 5.76561341 | -1.654780719 | H | 2.801577171 | 6.099050498 | -2.310890969 |
| C | 2.066740849 | 6.060251851 | -0.300077367 | H | 2.904820443 | 6.622011627 | 0.098653419 |
| C | 1.06207179 | 5.611409824 | 0.543635813 | H | 1.130773425 | 5.808254274 | 1.608899078 |
| C | -0.022219347 | 4.88179877 | 0.05257306 | H | 0.04870545 | 4.227218595 | -3.947382213 |
| C | 0.966923204 | 4.751696785 | -3.685792974 | H | -1.781928042 | 3.781759162 | 0.488495811 |
| C | -0.999585059 | 4.28907315 | 1.052550641 | H | 0.941199503 | 5.787399966 | -5.58815133 |
| C | 1.054776208 | 6.033748511 | -4.52833602 | H | 2.026706153 | 6.518232371 | -4.398416314 |
| C | 2.139573207 | 3.826723306 | -4.046566165 | H | 0.279222974 | 6.752574994 | -4.258567213 |
| C | -0.292459177 | 3.229794563 | 1.909918235 | H | 2.124781759 | 3.610533131 | -5.119248742 |
| C | -1.637140559 | 5.342605184 | 1.967268303 | H | 2.082025365 | 2.884295741 | -3.501811998 |
| H | 0.256264823 | -2.804590897 | -1.333111036 | H | 3.094177124 | 4.307999311 | -3.812694427 |
| H | -2.070712609 | 0.494261941 | 0.337100135 | H | -1.011139915 | 2.74590289 | 2.578634722 |
| H | 0.273043117 | 0.351785742 | 1.671235373 | H | 0.49157951 | 3.685682446 | 2.521801 |
| H | 1.704821597 | -1.67775309 | 0.643342634 | H | 0.160449246 | 2.462882889 | 1.281272324 |
| H | -0.441896089 | 0.184953844 | -3.832137345 | H | -2.142508378 | 6.126464459 | 1.400651662 |
| H | 1.22888354 | 2.597706346 | -0.605496171 | H | -0.880710892 | 5.816454603 | 2.599647099 |
| H | 2.966934042 | 0.647721868 | -1.173991388 | H | -2.370473954 | 4.867117329 | 2.62542423 |

Coordinates of Optimized Structures of **$Fe(C_5H_5)_2^+$** with TPSSh level of theory

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fe | 0.368760352 | 6.74324E-07 | -2.191679985 | C | 1.176268616 | 1.751445344 | -1.391284324 |
| C | -0.43876241 | -1.751442454 | -2.992067562 | H | -0.423489162 | -2.698331232 | -2.472930093 |
| C | 1.808620771 | -0.351782017 | -0.710031197 | H | 2.353759441 | -1.280269442 | -0.624947521 |
| C | 0.601880072 | -1.229577822 | -3.815765643 | H | 1.533430677 | -1.722127978 | -4.050689441 |
| C | -1.466704876 | -0.77641661 | -2.909819613 | H | -2.358137022 | -0.848836153 | -2.303981986 |
| C | 0.529595759 | -0.07771587 | -0.144284193 | H | -0.052674086 | -0.752713666 | 0.464719198 |
| C | 2.204220514 | 0.776426118 | -1.473535641 | H | 3.095660494 | 0.848860204 | -2.079364651 |
| C | 0.207924495 | 0.077707443 | -4.239077206 | H | 0.790194313 | 0.752691507 | -4.848095778 |
| C | -1.071096446 | 0.351785647 | -3.673326455 | H | -1.616223291 | 1.280278383 | -3.758410381 |
| C | 0.135630724 | 1.229569116 | -0.567588745 | H | -0.795927583 | 1.72210627 | -0.332669872 |

| | | | |
|---|---|---|---|
| H | 1.160998076 | 2.698342537 | -1.910409875 |

Coordinates of Optimized Structures of **Fe($C_5H_5$)$_2$** with TPSSh level of theory

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fe | 0.368759182 | -9.04087E-07 | -2.19167781 | H | -0.376876011 | -2.685934346 | -2.447113011 |
| C | -0.390326935 | -1.729683801 | -2.949454551 | H | 2.308348834 | -1.30896683 | -0.653692777 |
| C | 1.759781798 | -0.38400138 | -0.755763501 | H | 1.555163907 | -1.716141601 | -4.057005072 |
| C | 0.632207726 | -1.216584779 | -3.801147793 | H | -2.308994608 | -0.818113212 | -2.244369069 |
| C | -1.412564809 | -0.740923634 | -2.842154884 | H | -0.079798852 | -0.753222179 | 0.466007358 |
| C | 0.496156671 | -0.089794066 | -0.162437031 | H | 3.046527647 | 0.818073319 | -2.138965358 |
| C | 2.150089074 | 0.740903943 | -1.541189886 | H | 0.817283997 | 0.753247974 | -4.849354918 |
| C | 0.241340635 | 0.089804831 | -4.220914543 | H | -1.570857872 | 1.308956324 | -3.729633617 |
| C | -1.022279516 | 0.383996489 | -3.627574355 | H | -0.817639236 | 1.716173908 | -0.326382752 |
| C | 0.10531263 | 1.21660154 | -0.582225525 | H | 1.114431395 | 2.685927229 | -1.936270713 |
| C | 1.127863773 | 1.729681173 | -1.433921153 | | | | |

# UV-Vis Spectroscopy

## UV-Vis Spectroscopy of **1a** and **1b**

The UV-Vis spectra of 1.0 mM **1a** and **1b** in MeCN were recored using 1.0 mm diameter UV-Vis cell and Cary 6000i UV-Vis-NIR machine.

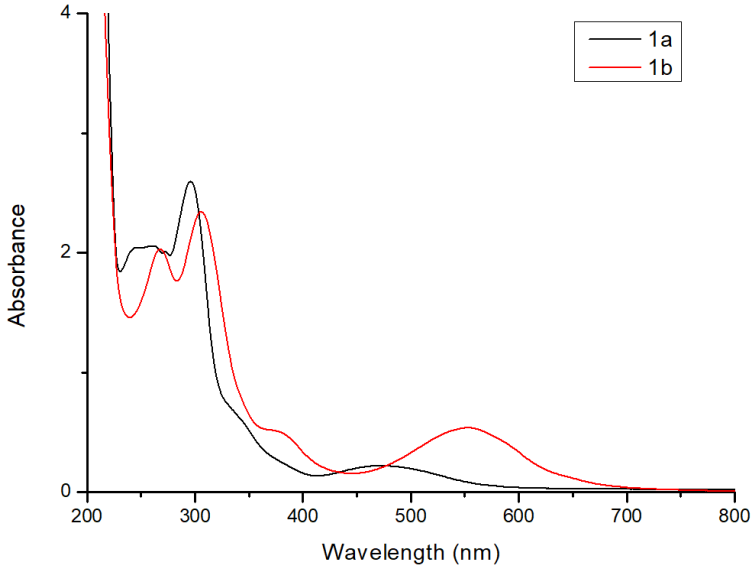



**Figure S10**. UV-Vis Spectra of **1a** and **1b** in MeCN at room temperature.

## UV-Vis Spectroscopy of **2a** and **2b**

In a $N_2$ atmosphere glovebox, **1a**/**1b** (3 mg) and $KC_8$ (1.2 eq.) were placed in a 4 mL vial and subsequently toluene (4 mL) was added to the vial. The reaction mixture was stirred at room temperature. After 30 min, the solution color was changed to deep green/purple. After celite filtration of the crude solution, the UV-Vis spectra of the solution of **2a** and **2b** in toluene were

recored using 1.0 mm diameter 'sure-sealed' UV-Vis cell and Cary 6000i UV-Vis-NIR machine. The decomposition of **2a** and **2b** was monitored under inert condition at room temperature.

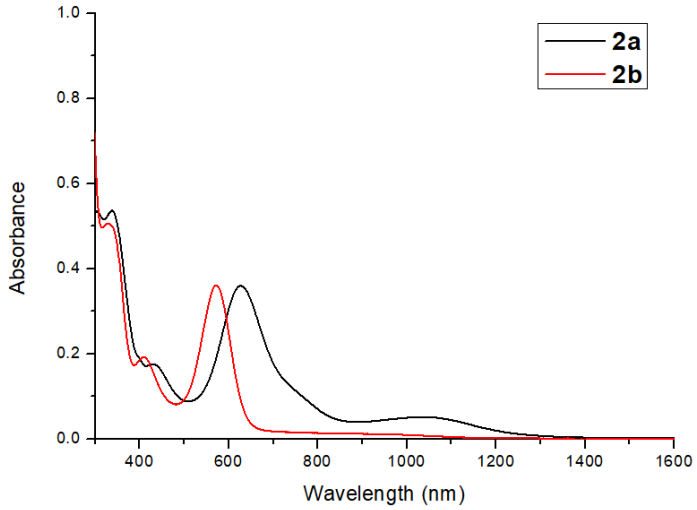



**Figure S11**. UV-Vis-NIR spectra of **2a** and **2b** in toluene at room temperature.

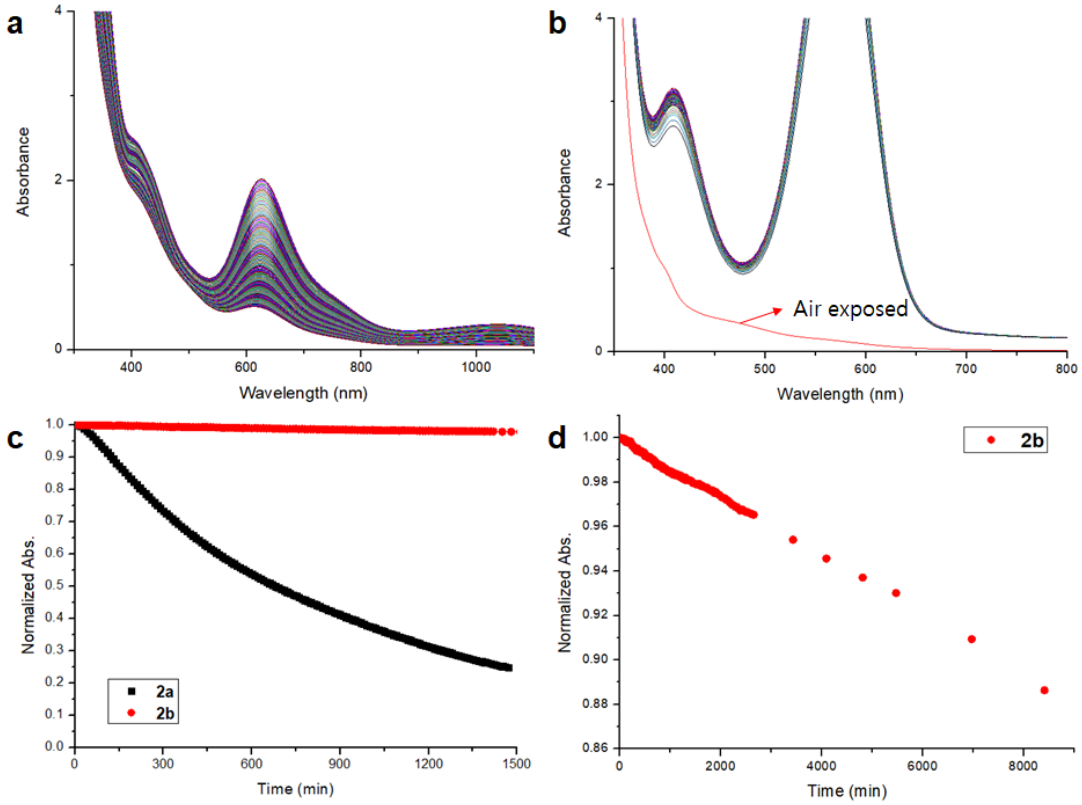



**Figure S12**. Decomposition monitoring UV-Vis-NIR spectra of (a) **2a** and (b) **2b** in toluene at room temperature.

## Electrochemistry

General Methods

The solutions were prepared and the electrochemical tests were performed in an Ar-filled glove box under an inert atmosphere (<0.5 ppm $O_2$, $H_2O$). In the CV tests, a three-electrode system (Pt counter electrode, $Ag/AgNO_3$ reference electrode, 3.0 mm glassy carbon working electrode) was employed with a scan rate of 100 mV $s^{-1}$. In the flow cell test, a custom flow cell with backing plates (polyethylene-coated fiber glass), flow fields (polytetrafluoroethylene (PTFE)), and gaskets (PTFE) was fabricated using materials purchased from ILDO F&C (Korea). The flow cells were assembled with carbon felts (XF30A; TOYOBO, Korea) as electrodes at both the anode and cathode side with four pieces of microporous separators (Celgard 4560) sandwiched in between. The active size of the flow cell was 2.0-cm wide × 2.0-cm long (4 $cm^2$), and norprene tubing (Masterflex) was used. The electrolytes (7 mL on each side) containing DMPZ (0.03 M) and **1b** (0.03 M) in the supporting electrolyte of 0.5 M LiTFSI in MeCN were flowed through the felt electrodes at a flow rate of 80 mL $min^{-1}$ using a peristaltic pump (Col-Parmer). Flow cell test was performed at room temperature in constant-current mode using a battery test system (WBCS 3000; WonA Tech, Korea). The volumetric capacity was calculated based on the volume of anolyte (7 mL).

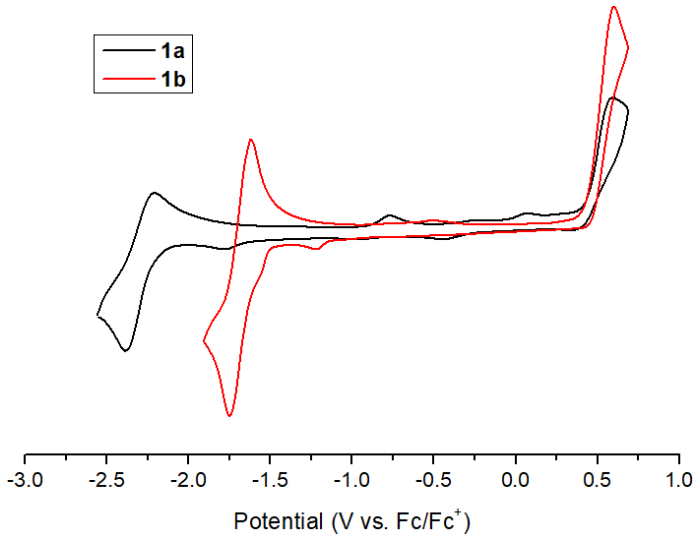



**Figure S13**. Cyclic voltammograms of **1a** and **1b** in 0.1 M of $[Bu_4N]PF_6$/MeCN (vs. $Fc/Fc^+$, scan rate = 0.1 V/s).

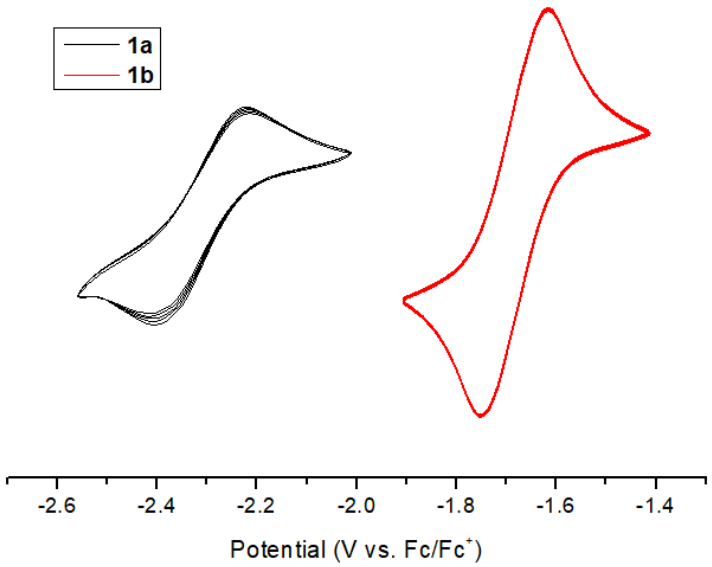



**Figure S14**. Decomposition in cyclic voltammogram in 0.1 M of $[Bu_4N]PF_6$/MeCN (vs. $Fc/Fc^+$, scan rate = 0.1 V $s^{-1}$, **1a**: 5 cycles, **1b**: 15 cycles)

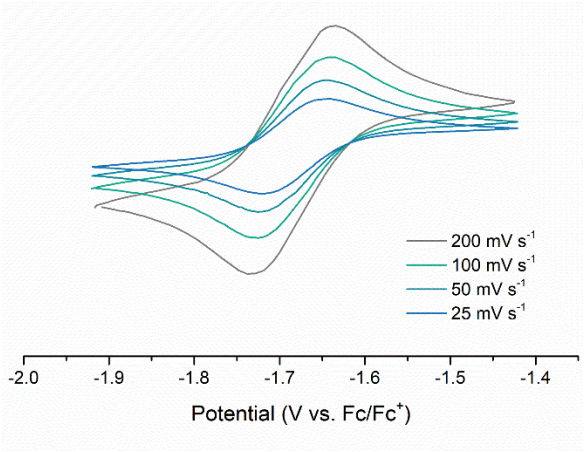



**Figure S15**. Scan rate-dependence cyclic voltammetry study for **1b**.

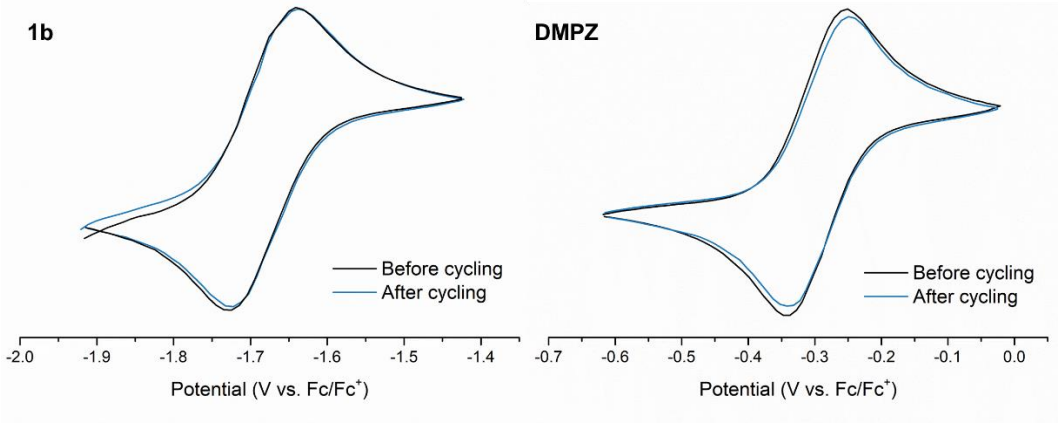



**Figure S16**. Cyclic voltammograms of anolyte (**1b**, left) and catholyte (DMPZ, right) before and after cycling.

## Electron paramagnetic resonance

General Methods

EPR spectra were recorded on a Bruker X-band A200 spectrometer. Spectra processing and simulation were performed with Bruker WIN-EPR and EasySpin associated with DFT calculations. [18] EPR computation of **2a** and **2b** for isotropic hyperfine coupling constants were performed with above computation results, and rescaled to fit the experimental data.

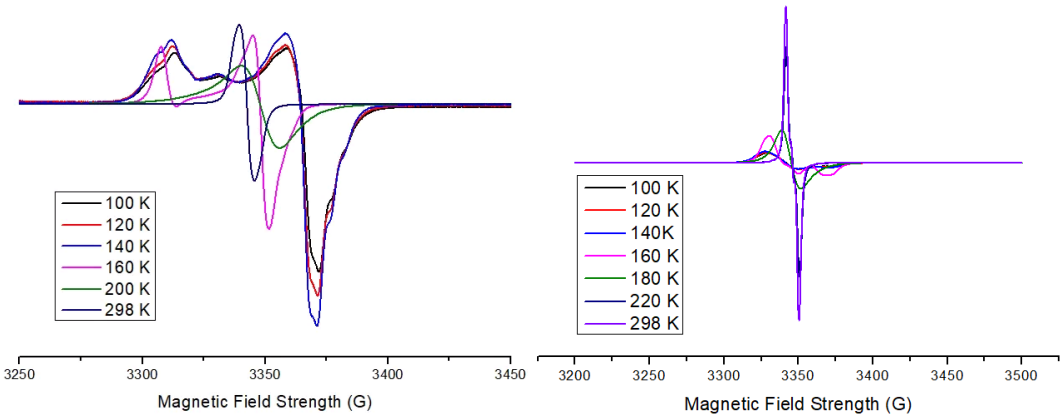



**Figure S17.** X-band of variable-temperature electron paramagnetic resonance of **2a** and **2b** in toluene.

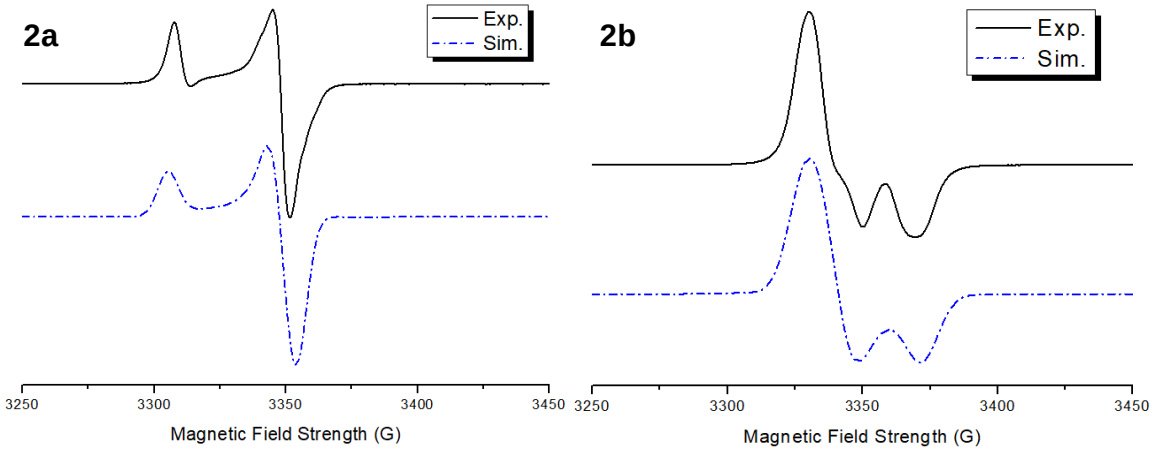



**Figure S18.** Simulated at 160 K (a) υ = 9.438481 GHz; $g_1$ = 2.04025, $g_2$ = 2.01422, $g_3$ = 2.01015; A(Fe) = 26.9724 MHz, A(C) = 5.58228, 6.80675, 11.822, 136.875 MHz, A(N) = 1.82653, 2.36883 MHz; Gaussian line width = 0.746646 mT. (b) υ = 9.441988 GHz; $g_1$ = 2.0269, $g_2$ = 2.019, $g_3$ = 2.0003; A(Fe) = 77.8224 MHz, A(C) = 39.5427, 39.9911, 162.672 MHz, A(N) = 8.64382 MHz; Gaussian line width = 1.06745 mT.

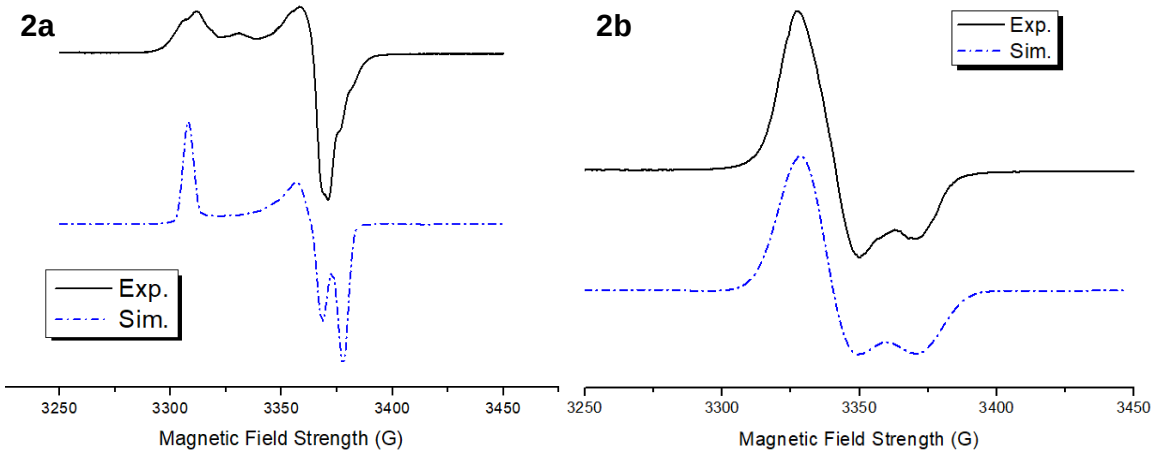



**Figure S19.** Simulated at 140 K (a) υ = 9.439248 GHz; $g_1$ = 2.03868, $g_2$ = 2.000343, $g_3$ = 1.99643; A(Fe) = 54.908 MHz, A(C) = 5.65412, 7.78712, 15.3831, 211.175 MHz, A(N) = 1.35926, 3.49318 MHz; Gaussian line width = 0.4 mT. (b) υ = 9.440176 GHz; $g_1$ = 2.0263, $g_2$ = 2.0204, $g_3$ = 1.9998; A(Fe) = 20.1334 MHz, A(C) = 23.8474, 18.0267, 298.6589 MHz, A(N) = 8.4724 MHz; Gaussian line width = 1.5937 mT.

## $^{57}$Fe Mössbauer spectra

Mössbauer spectra were recorded on a spectrometer from SEE Co. (Edina, MN) operating in the constant acceleration mode in a transmission geometry. The sample was kept in an SVT-400 cryostat from Janis (Wilmington, MA). The quoted isomer shifts are relative to the centroid of the spectrum of a metallic foil of α-Fe at room temperature. Frozen benzene solution samples were prepared by freezing the sample in a Delrin cup. All samples were prepared within a glovebox with rapid transfer to a liquid nitrogen bath before mounting in the cryostat. Data analysis was performed using the program WMOSS (www.wmoss.org) and quadrupole doublets were fit to Lorentzian lineshapes.

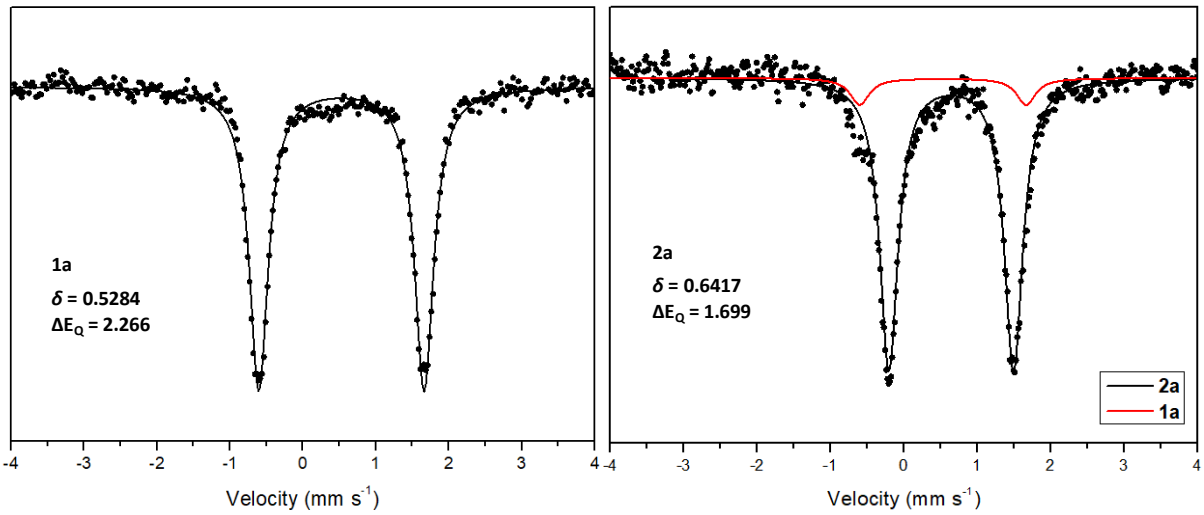



**Figure S20.** $^{57}$Fe Mössbauer spectrum of **1a** (left) and **2a** (right) (80 K, 50 mT parallel, benzene);

Residual **1a** (8.7%) is assigned in the $^{57}$Fe Mössbauer spectrum of the benzene solution of **2a**.

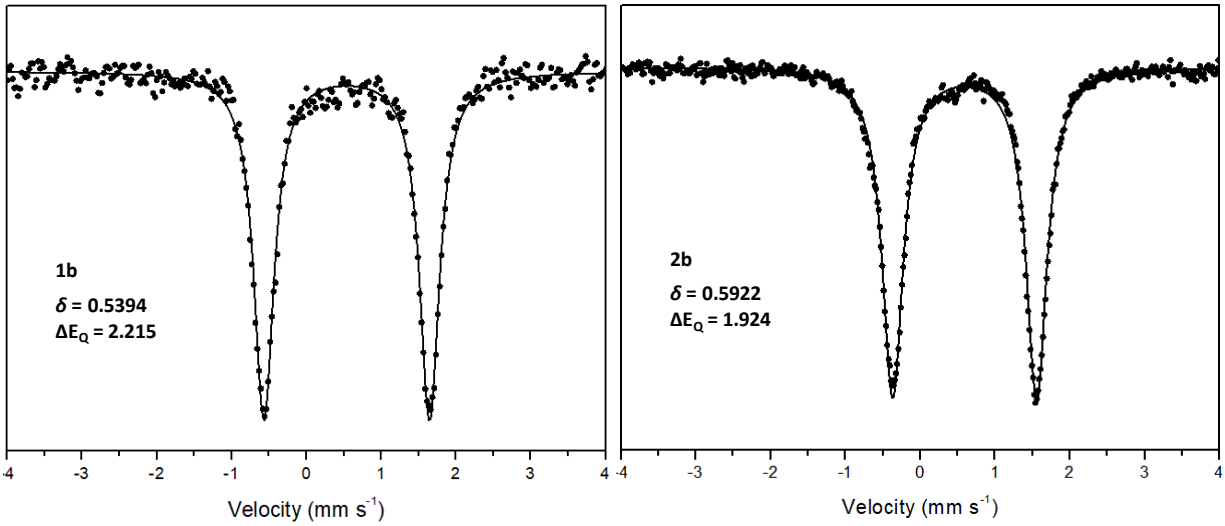



**Figure S21.** $^{57}$Fe Mössbauer spectrum of **1b** (left) and **2b** (right) (80 K, 50 mT parallel, benzene).

## FT-IR Spectroscopy

Infrared spectra were obtained as thin films formed by evaporation of THF solutions (**1a**, **1b**) and ether solutions (**2a**, **2b**) on KBr windows using a Bruker Alpha system.

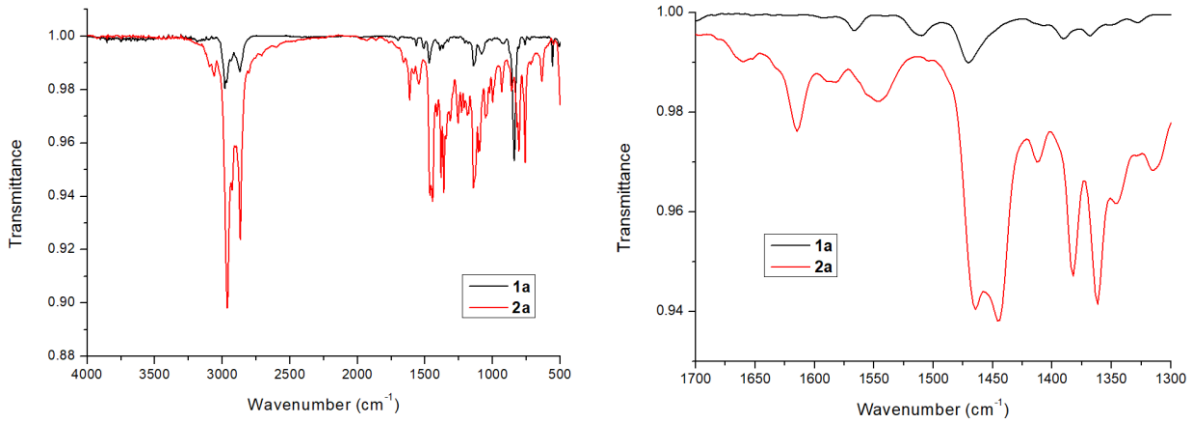



**Figure S22.** FT-IR spectra of **1a** and **2a**.

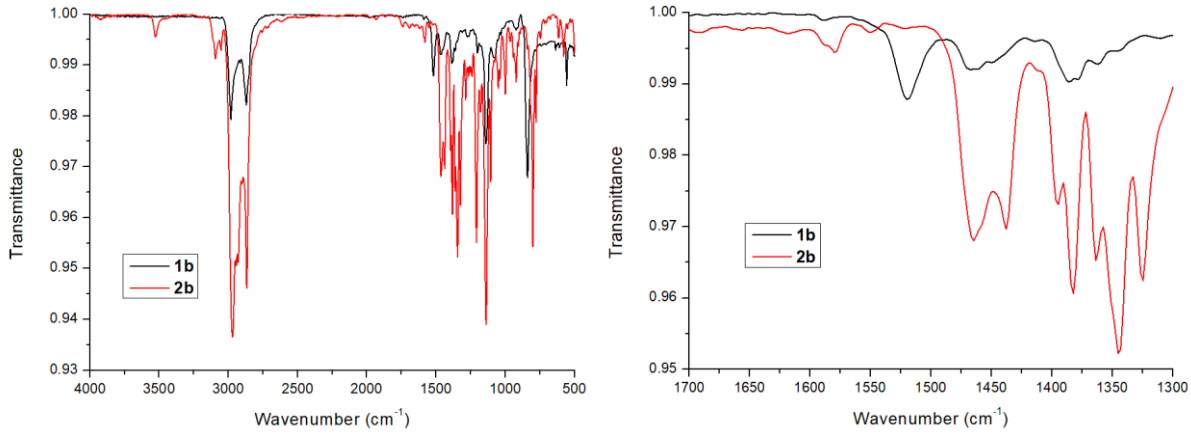
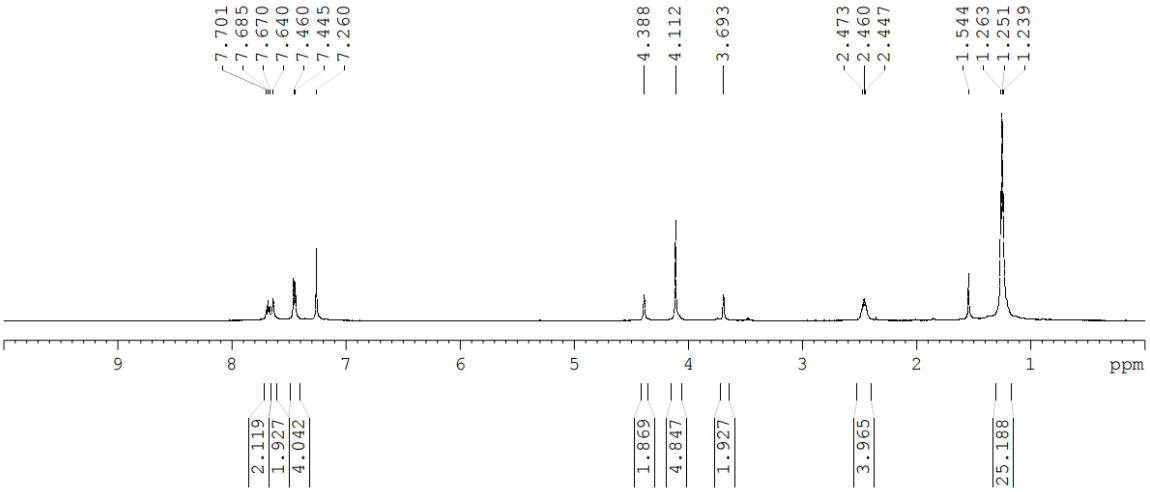



**Figure S23.** FT-IR spectra of **1b** and **2b**.

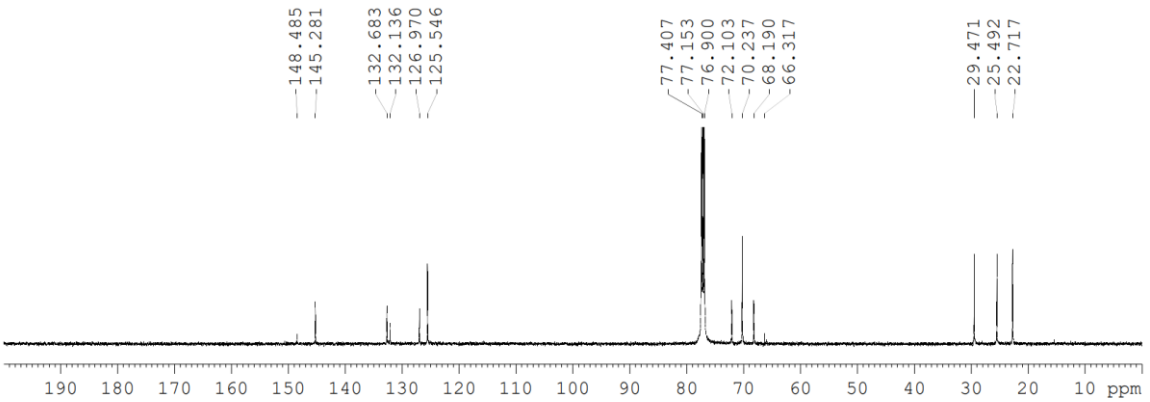
# NMR Spectroscopic Analysis

### NMR Spectra of 1a

$^{1}$H-NMR in $CDCl_3$

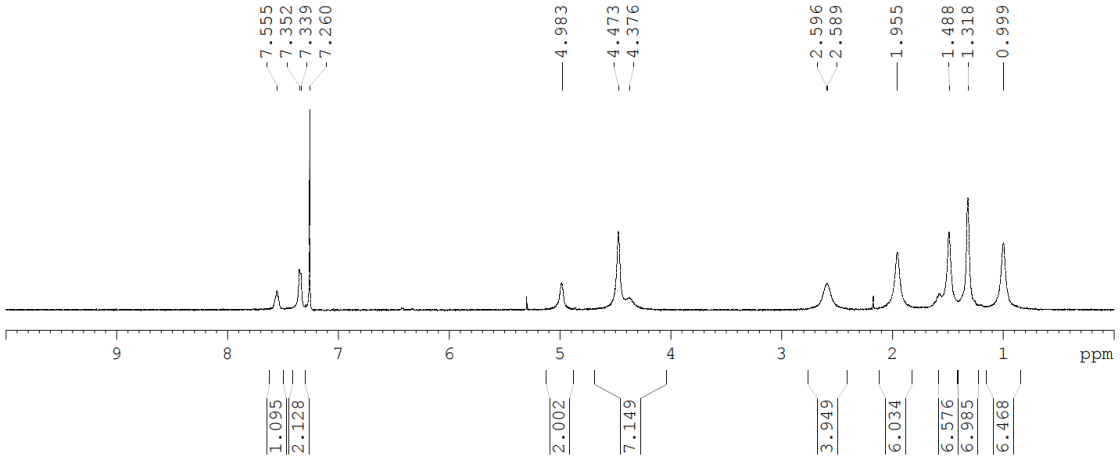



$^{13}$C-NMR in $CDCl_3$

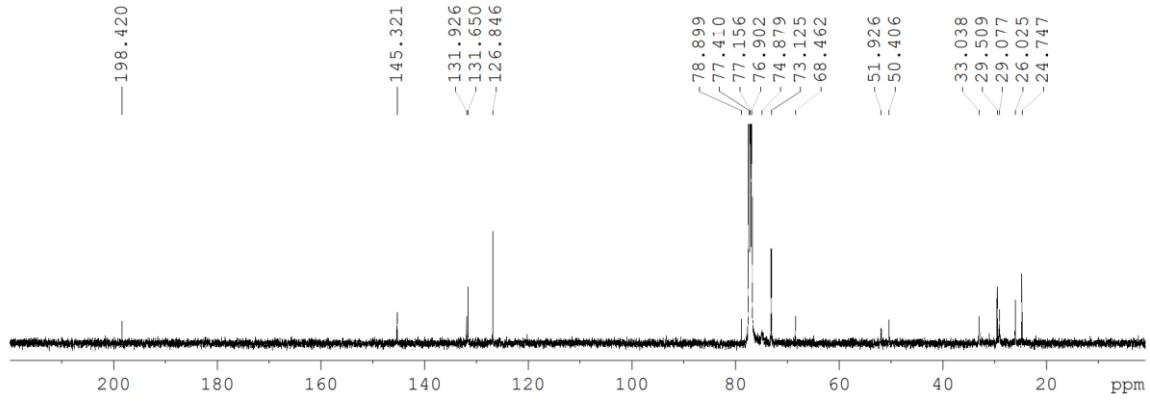


**NMR Spectra of 1b**

$^{1}$H-NMR in $CDCl_3$




$^{13}$C-NMR in $CDCl_3$



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